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Pyrolysis of Industrial Wastes for Oil and Activated Carbon Recovery

Occidental Research Corp, La Verne, Calif

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16. ABSTRACT

The Occidental Research Corporation (formerly Garrett Research and Development Company, Inc.) has developed a new Flash Pyrolysis process which can produce up to two barrels of synthetic fuel oil from a ton of dry cellulosic solids. This report presents the results of a four-phase laboratory, pilot plant, product evaluation and engineering evaluation program to study the pyrolytic conversion of Douglas fir bark, rice hulls, grass straw and animal feedlot waste to synthetic fuel oil and char. With the use of an existing 4 ton/day pilot plant, good quality products were obtained from all feedstocks except animal waste. A wax by-product was obtained from the pyrolysis of fir bark and grass straw. Excellent pilot plant material balances were obtained for oil production runs on Douglas fir bark and rice hulls, and these were satisfactorily combusted in a standard test boiler. Similar yields were obtained from semi-quantitative runs using grass straw. The pyrolytic chars from tree bark and rice hulls were evaluated as a source of activated carbon, and tree bark char was satisfactorily compressed to produce excellent quality charcoal briquettes.

The economic evaluation shows that a 1200 dry ton/day tree bark conversion plant could be built and operated with a profit of about $10/ton of dry bark. The breakeven point for this process to produce synthetic fuel oil and char for briquettes appears to be 300 dry tons of bark/day.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

"Pyrolysis of Industrial Wastes for Oil and Activated Carbon Recovery" presents the results of pilot plant operations that pyrolysed four industrial residues and produced fuel oil and usable charcoal carbon. An economic evaluation indicated that a 1200-ton-per-day tree bark conversion plant could be built and operated with a profit of $10 per ton of dry bark. Rice hulls and grass straw produced similar results. For further information, contact the Food and Wood Products Branch, IERL-Ci.

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ABSTRACT

The Garrett Research and Development Company has developed a new flash pyrolysis process that can produce up to two barrels of synthetic fuel oil from a ton of dry cellulosic solids. This report presents the results of a four-phase laboratory, pilot plant, product evaluation, and engineering evaluation program to study the pyrolytic conversion of Douglas fir bark, rice hulls, grass straw, and animal feedlot waste to synthetic fuel oil and char for either briquettes or powdered activated carbon. Using an existing 4-ton-per-day pilot plant, good quality products were obtained from all feedstocks except animal waste, which has objectionably high concentrations of nitrogen, sodium, and potassium. An interesting wax byproduct was obtained from the pyrolysis of fir bark and grass straw. Excellent pilot plant material balances were obtained for oil production runs on Douglas fir bark and standard test boiler. Semiquantitative pilot plant runs on grass straw indicated that similar yields of oil and char can also be expected from this feedstock. The pyrolytic chars from tree bark and rice hulls were evaluated as a low cost source of activated carbon, but equipment limitations led to rather poor results. However, tree bark char was satisfactorily compressed to produce excellent quality charcoal briquettes.

The economic evaluation shows that a 1200-dry-ton-per-day tree bark conversion plant could be built for $13.3 million (excluding land) and operated for $2.9 million per year, including amortization, with a profit of about $10 per ton of dry bark. The break-even point for this process to produce synthetic fuel oil and char for briquettes appears to be 300 dry tons of bark per day.

This report was submitted in fulfillment of Grant R-801202 by Occidental Research Corporation (formerly Garrett Research and Development Company, Inc.) under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period August 1972 to March 1975, and work was completed as of March 1975.

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The Georgia Pacific Corporation paid for 40 tons of shredded Douglas fir bark and the Crown Zellerbach Corporation paid for its transportation from Northern California to the Garrett pilot plant facilities in La Verne, California. The Rice Growers Association of California paid for the milling and transportation of 20 tons of rice hulls and supplied valuable consultation regarding utilization of this waste product. The Oregon Seed Council paid for the transportation of 10 tons of rye grass straw. The World Farm Foundation provided samples of dried animal feedlot wastes. The Northwest Natural Gas Company provided consultation advice throughout the course of this program regarding markets for synthetic fuels. Finally, the State of Oregon and the City of Portland, Oregon provided supplemental financial assistance in return for a slight increase in the scope of work in order to provide synergistic information regarding the conversion of the organic portion of municipal refuse to synthetic fuels. The assistance of these organizations is greatly appreciated.

SECTION I

INTRODUCTION

The Garrett Research and Development Company has developed a new flash pyrolysis process which can produce over two barrels of synthetic fuel oil from a ton of dry cellulosic solids. Preliminary tests showed that the residual char from pyrolysis of homogeneous feedstocks such as tree bark and rice hulls may also be valuable as a source material for powdered activated carbon. Garrett Research built and has successfully operated a four ton per day pilot plant for studying this pyrolysis process on coal and on solid wastes. Certain industrial wastes, as well as coal and municipal waste, have also been pyrolyzed to produce synthetic fuel oil and char in a smaller bench scale laboratory reactor. Based on the pilot plant and bench scale reactor results, a proposal was submitted to the Environmental Protection Agency in March, 1972 to investigate the pyrolysis of tree bark, animal feedlot waste, rice hulls and grass straw using the Garrett process. In June 1972, EPA awarded Grant R-801202 in order to conduct a four phase program covering laboratory pyrolysis studies, pilot plant studies, product evaluation studies, and finally, an economic feasibility and preliminary process design study.

The first effort of this program was initiated in August 1972, and was based upon the proven premise that by employing a short residence time process such as the Garrett Flash Pyrolysis system, substantially higher liquid fuel yields can be obtained from carbonaceous solids than had heretofore been observed. Additionally, due to very rapid heat transfer conditions, the resulting byproduct char tended to possess a much larger surface area than chars produced by slower, conventional fixed-bed or fluid-bed processes. The purpose of this EPA program was to demonstrate on a modestly sized pilot plant basis, the economic and technical viability of employing this process for converting large volumes of waste materials to saleable products which would possess a wide market potential.

SECTION II

CONCLUSIONS

1. High yields of synthetic fuel oil were obtained from rice hulls, animal feedlot waste, Douglas fir bark and grass straw in a single, short residence time bench scale pyrolysis reactor and confirmed in the four ton per day pilot plant. The yields were:

a) Grass straw = 30 to 50%
b) Douglas fir bark = 35 to 50%
c) Rice hulls = 25 to 40%
d) Animal waste = 30%

The yields were not sensitive to pyrolysis temperatures in the temperature range 420 to 540°C (785 to 1005°F) except for Douglas fir bark, where increased temperatures resulted in higher oil yields, an optimum being about 510°C (950°F).

2. The pyrolysis of Douglas fir bark yielded approximately 5 wt % of wax as a crude by-product of the oil collection system. It was found that this wax could be extracted from the pyrolytic oil during the normal quench procedure using a relatively inexpensive paraffinic quench oil that is immiscible with the non-wax portion of the pyrolytic product oil. In several respects, this crude wax product was similar to that obtained by commercial Douglas fir bark solvent extraction operations. A similar waxy product was also found in the grass straw oil.

3. Good quality oil was obtained from all feedstocks except animal feedlot waste, which yielded oil containing 5 to 7% nitrogen -- unacceptably high for a boiler fuel. In addition, the char from animal waste contained excessive amounts of sodium and potassium. The disposal of raw animal waste using the Garrett Flash Pyrolysis process is therefore not considered feasible without additional pretreatment. For this reason animal feedlot waste was deleted from the pilot plant phase of the contract program.

4. Based upon the results of the laboratory phase, operating conditions for the pilot plant phase employing an existing four ton per day facility were established for Douglas fir bark, rice hulls and grass straw.

5. Excellent and accurate pilot plant results were obtained during oil production runs. Two measures of pilot plant accuracy are available: material balance closure of carbon and hydrogen, and comparison of char yields by two independent methods. The elemental material balances strongly support the overall validity of these results. Average closures of C, H, and O balances for the tree bark runs were respectively 96%, 97% and 104%. Similarly, the closures for the rice hull runs were 99%, 100% and 100%. The statistic char-yield-by-difference compares favorably with the char yield from the char production runs when only electrical heaters on the reactor were used for heat input. On a moisture and ash free basis, the by-difference yield for tree bark char was 22.4% compared to the direct measurement value of 22.3%.

6. Semi-quantitative pilot plant runs on rye grass straw indicate that good quality fuel oil and usable char could probably be produced. However, operating anomalies were encountered which suggest that either further tests, or a modest redesign effort would be required to handle this particular feedstock. These problems were tentatively attributed to the unusual and difficult flow characteristics of the resulting pyrolytic char.

7. An engineering process design and economic evaluation of the Garrett Flash Pyrolysis process was made for the conversion of Douglas fir bark to synthetic fuel oil and saleable char products. The design calculations and cost estimates were prepared for two commercial size plants using the pilot plant data obtained in Phase II and the evaluations of the oil and char as marketable products described in Phase III.

The pyrolysis plant economics were estimated for feed rates of 300 and 1200 tons per day (oven dry basis). The products considered are a low sulfur tree bark oil suitable for use as a utility boiler fuel or as a blend with No. 6 fuel oil in a utility boiler; and char which is marketable as either a solid fuel, as charcoal briquettes or as a source of inexpensive, powdered, activated carbon.

The economic evaluation shows that a commercial plant sized to process 300 tons per day (dry) of tree bark will cost $5.0 million and have an annual operating cost of $1.7 million, i.e. about $21 per ton, including plant amortization. This size plant is expected to break even when the char is sold as briquettes. A 1000-ton-per-day plant, producing similar products, shows a good return on investment with a profit of about $10 per ton of dry bark. The plant will cost $13.3 million and have an annual operating cost of $2.9 million, i.e. about $10 per ton, including plant amortization.

SECTION III

RECOMMENDATIONS

1. Based on the very favorable economics projected by this program, immediate steps should be initiated to fund the construction of a 300 to 1200 ton per day prototype pyrolysis plant to convert wood wastes to synthetic fuel oil and char for briquettes.

2. Since higher oil yields might be obtained from Douglas fir bark at higher pyrolysis temperatures, this should be investigated in a very brief bench scale program.

3. Because high oil yields can be expected from grass straw, the operating anomalies experienced in handling this light, fluffy material should be investigated further and effective operating techniques and design should be sought for this feedstock.

4. The animal feedlot waste feedstock yielded synthetic oil and char of unacceptable quality. Because of the intense interest in finding an economical solution for the animal feedlot waste problem, serious considerations should be given to combining a protein recycling process with the Garrett pyrolysis operation. Such a combination, if successful, could result in about half of the manure's dry weight being recycled as a 20-35% protein feed, with the remaining half pyrolyzed to produce an acceptable synthetic fuel oil and a relatively low-ash char.

5. Owing to the high potential value of the wax obtained in the pyrolysis of Douglas fir bark, further studies should be made to determine the steps required to separate and purify this wax to obtain a saleable non-fuel product.

SECTION IV

PHASE I - LABORATORY PYROLYSIS STUDIES

INTRODUCTION

Phase I of the study of the pyrolysis of industrial waste presents the results of a laboratory evaluation program. A five pound per hour bench scale pyrolysis reactor was used to study the applicability of the Garrett flash pyrolysis process for the conversion of Douglas fir bark, rice hulls, grass straw and animal feedlot waste to synthetic fuel oil and activated carbon. The effects of pyrolysis temperature, feed moisture content and particle size on product yields and quality were determined in order to set optimum conditions for subsequent pilot plant operations using a four ton per day unit.

The results of the laboratory study indicate that over 80% of the volatile matter in each of the four feedstocks can be converted to synthetic liquid and gaseous fuels in a single, short residence time pyrolysis operation. Oil yields based on dry reactor feed were 30% from animal waste, 40% from rice hulls and 50% from grass straw. Oil yields from fir bark were 35 to 50% depending upon pyrolysis conditions. Good quality synthetic fuels were obtained from all feedstocks except animal waste, which yielded oil with 5 to 8% nitrogen and a by-product char containing high concentrations of sodium and potassium salts.

LABORATORY PYROLYSIS PROCEDURES

Feed Preparation

Feedstocks for the laboratory pyrolysis phase were provided by several private organizations as contributions to the program.

Size analyses of the four feedstocks were of significant economic importance, but were often difficult to determine accurately. Tree bark and grass straw were especially troublesome since these materials tended to ball up during dry screening operations due to their fibrous nature when milled to fine particle sizes. In the latter part of the laboratory pyrolysis program, sedimentometer analyses were performed on the feeds and product chars, and the size distributions thus obtained always indicated smaller particles than the dry screening procedure.

Rice Hulls -

Ninety kg (200 lb) of rice hulls was obtained from the milling of Calrose medium grain rice grown in the Sacramento valley. The material received had a moisture content of 6.4% and was essentially all minus 0.3 cm (1/8 inch) in size. About 34 kg (75 lb) was shredded using a 40 hp Rietz RD-12 disintegrator with a 1/16th inch screen. The resulting material was 95% minus 30 mesh and was then dried under nitrogen for 24 hours at 110°C. This material was used in pyrolysis runs 372-08 and 372-10.

Another 34 kg of the as-received rice hulls was similarly shredded with the Rietz disintegrator and then further reduced in size by Vortec, Inc. of Los Angeles using their Model M-1 Impact Mill and Model C-1 Air Classifier in series. The material was estimated by Vortec to be approximately 70% minus 200 mesh and was then dried in the same manner as described above. This finely divided material was used as feed for pyrolysis runs 372-14, 372-16, 372-18 and 372-20.

A subsequent shipment was received from the same source and shredded in the Rietz disintegrator followed by further shredding in a MikroPulverizer using a #010 screen, to substantially under 200 mesh. At this point the material contained 6.8% moisture, and it was used as the feed in runs 372-34 and 372-48 without further drying.

Animal Waste -

Ninety kg (200 lg) of animal feedlot waste was obtained from a dairy farm in the Chino valley of southern California. The material received had a moisture content of 11.8% and was minus 0.6 cm (1/4 inch) in size. Thirty-four kg (75 lb) was shredded in the Rietz disintegrator and further processed by Vortec, Inc. in the same manner as the rice hulls, resulting in material which was approximately 70% minus 200 mesh. This material was dried at Garrett Research under nitrogen for 10 hours at 90°C and was used as feed in runs 372-22, 372-24 and 372-28.

The remaining animal waste was later milled in a MikroPulverizer with a #010 screen and further screened to produce about 29 kg (65 lb) of minus 200 mesh material. This was dried under nitrogen for 24 hours at 90°C and used as feed in runs 372-40 and 372-46.

Tree Bark -

Ninety kg (200 lb) of minus 0.6 cm (1/4 inch) Douglas fir bark was shipped to Garrett Research from northern California. The material received had a moisture content of 18%. Thirty-four kg (75 lb) was shredded in the Rietz disintegrator and processed by Vortec, Inc. as described above. It was then dried under nitrogen and used as the feed for runs 372-26 and 372-30.

A subsequent larger shipment of bark from the same source was dried in a fluid-bed unit and then shredded in the Rietz disintegrator for pilot plant operations. Some of this material was screened to obtain about 11 kg (24 lb) of minus 24 mesh material. This was further dried under nitrogen for runs 372-32 and 372-44.

Grass Straw -

One hundred twenty-five kg (275 lb) of annual rye grass straw from the Willamette Valley was received unshredded. About 34 kg (75 lb) was shredded in a MikroPulverizer with a 1/4 inch screen and a #46 punch screen. The resulting material, minus 6 mesh, was further processed by Vortec, Inc. in their impact mill and air classifier system to produce 23 kg (50 lb) of material which dry screening showed to be 50% minus 200 mesh. Vortec experienced difficulty in milling the grass straw and could process the material at only one-third the usual rate, due to (a) low particle density diminishing the effectiveness of the impact mill, (b) long stringy particle shape, with L/D up to 20 persisting after several passes through the mill, and (c) electrostatic charges on the particles. This material was dried under nitrogen in the same manner as the other feeds, and used in runs 372-36, 372-38 and 372-50.

Bench Scale Pyrolysis System

The apparatus used for pyrolysis experiments in the laboratory phase consisted of a vibrating screw feeder, a reactor, three cyclone separators, a glass condenser train, and a gas sampling system. Several modifications were made to the previously existing collection system to improve the accuracy of the results. Some improvements which were made during the laboratory phase are described below.

Gas Sampling

The gas sampling train provides a time-averaged sample for analysis by mass spectrometry and gas chromatography. In the earlier runs this was accomplished by drawing several (usually five) equal increments of reactor off-gas into a 240 cc glass sample bulb by draining a Na_2SO_4/H_2SO_4 buffer solution from the bulb at equally spaced times during the run. The system and its operating procedure were described in detail in an unpublished progress report (GR&D 72-038-1, October 1, 1972).

Usually two 250 cc gas sample bulbs were filled using this technique, and both were analysed. Occasionally the two analyses conflicted significantly. This could have been caused by uneven feeding, since bridging and clumping of the fibrous feed materials at the feeder unit had been observed previously. In an effort to obtain a more accurate time-averaged sample, the gas sampling train was modified after run 372-30. For all subsequent runs a bleed stream of gas was drawn continuously and at a constant rate into a previously evacuated #3 gas cylinder. Two cylinders were filled, each continuously over half the duration of the run. This modification resulted in improved consistency between the first-half and second-half gas analyses, and the gas compositions reported for run 372-32 and subsequent runs are considered more reliable than those for the earlier runs.

H_2O/H_2S Sampling -

At the beginning of the program it was recognized that concentrations of H_2O and H_2S in a gas sample are not readily determined by mass spectrometry. A separate sampling train was therefore used for these two components, consisting of an aerosol filter, a Drierite column and a $CuSO_4$/Drierite column. This train and its operation were also described in the monthly progress report GR&D 72-038-1.

The Drierite column typically absorbed 0.5 to 2 g H_2O during a three hour run, while the $CuSO_4$/Drierite column absorbed 0.05 to 1 g H_2S. The concentration of water vapor was usually substantially higher than the concentration of hydrogen sulfide, so that a small amount of breakthrough of water from the Drierite trap into the H_2S trap could increase the apparent H_2O concentration dramatically without decreasing the apparent H_2O concentration enough to be noticeable. That such an event was happening was suspected upon examination of results from some of the earlier runs. The remedy was to add a second Drierite column after the first as a guard trap. For runs where the second Drierite column showed a very small weight increase compared to the first, it could be assumed that no H_2O was reaching the H_2S trap. Even with this improvement, however, gas composition from some of the later runs showed unreasonably high H_2S levels which were inconsistent with other runs using the same feed, and for which no obvious trend with temperature or other operating conditions could be determined.

Aerosol Sampling -

At the beginning of the program an electrostatic precipitator (ESP) was used to catch aerosol droplets which form when the hot oil vapor produced during pyrolysis is suddenly cooled. These aerosol droplets are often too small to be collected in the glass condenser train or in the five micron filter bag after the condensers. In bench scale pyrolysis tests, the amount of oil which forms as aerosol is often one-fourth to one-third of the total oil yield. It is therefore quite important to recover this aerosol in order to obtain meaningful results.

In analyzing the results of early runs, it was seen that the aerosol production indicated by the weight gain of the Pall and Gelman filters in the H_2O/H_2S sampling train usually exceeded by about 65% the amount of aerosol collected by the ESP. The conclusion was that the ESP was not collecting all the aerosol. Therefore the H_2O/H_2S sampling train data were used to calculate aerosol production in all runs, and the ESP was operated only for air pollution control and as a qualitative indication of aerosol production.

Pyrolysis Operations

Before the start of a pyrolysis run, the entire system was purged with inert gas to exclude oxygen. After the reactor system reached its operating temperatures, the vibrating screw feeder was started at a rate of 2 to 7 lb/hr, usually about 5 lb/hr. The reactor exit temperature was recorded by a thermocouple in the gas stream. This is referred to as the pyrolysis temperature hereafter.

The hot reactor effluent was passed through three cyclones to separate pyrolytic char from the gases. Pyrolytic oil and part of the pyrolytic water were then condensed in two water-cooled glass condensers and one cooled by liquid from a dry ice/methanol bath. Some of the oil aerosol was then caught by a five micron filter bag. Portions of the gas stream were then diverted to the gas sampling and H_2O/H_2S sampling trains, and the rest of the gas was passed through the electrostatic precipitator and an incinerator before venting to the atmosphere.

EXPERIMENTAL RESULTS

The results obtained from 21 runs carried out during the laboratory pyrolysis phase are reported in Tables I-1 through I-4.

Product Compositions

Pyrolysis of solid waste by the Garrett process yields four products -- char, oil, gas and water. However, these products are not completely separated by the bench scale apparatus collection train, as they are in the Garrett pilot plant and subsequent commercial plants. The procedures by which product yields and compositions given in Tables I-1 through I-4 were determined are discussed below.

Feed -

In every pyrolysis run, the feed material was routinely submitted to the Garrett analytical laboratory for proximate and ultimate analysis. These analyses revealed moisture contents up to 7%, depending on atmospheric conditions, the material's storage history, and intentional variations in moisture level. The moisture contents of the reactor feeds are given separately in Tables I-1 through I-4, and the analyses shown have been calculated on a dry basis.

Char -

The major part of the pyrolytic char product in each run was caught by the first of the three cyclones. Small amounts of char were also recovered from the other two cyclones and from the piping connecting the last cyclone and the glass condenser train. The weights of char from these locations were all reduced by their respective moisture contents as determined by proximate analysis, to arrive at "dry char." In addition, a small amount of char fines usually passed through all the cyclones into the glass collection train. The tarry liquids from the glass collection train were therefore analyzed for quinoline-insoluble contents as an indication of the char carryover. This contribution to the char yield was usually on the order of 1% of the total char yield, which was calculated as follows:

$$\text{Dry char yield} = \left(\frac{\text{Wt char in cyclones, dry basis} + \text{Wt quinoline-insoluble in glass train}}{\text{Wt feed, dry basis}}\right) \times 100\%$$

Table 5-1. LABORATORY PYROLYSIS RESULTS - RICE HULLS

Run Number Feed Rate Reactor Exit Temp.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Feed Analysis, wt % dry C H N S Ash O (Difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Feed Moisture, wt %	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Pyrolytic Char, dry % of dry feed wt Gross Heating Value, Btu/lb	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C, wt % H N S Ash O (Difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Pyrolytic Oil, dry % of dry feed wt Gross Heating Value, Btu/lb	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C, wt % H N S Ash O (Difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Pyrolytic Gas, dry % of dry feed wt Gross Heating Value, Btu/SCF	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Gas, mol %	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Pyrolytic Water[b], % of dry feed wt	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Total Products, % of dry feed wt	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[a] Calculated

[b] Excluding feed moisture

Table [illegible]. [illegible]

Run Number	372-22	372-24	372-38	372-40	372-45
Feed Size, Mesh	-200	-200	-200	-200	[illegible]
Reactor Exit Temp., °C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
°F	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Feed Analysis, wt.% Dry					
C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H	4.70	[illegible]	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
S	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cl	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ash	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
O (Difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00	100.00	100.00
Feed Moisture, wt.%	7.99	1.02	1.22	1.82	0.77
Pyrolytic Char, Dry % of dry feed wt.	25.6	35.4	48.1	52.0	46.0
Gross Heating Value, cal/g	3027	2990	3224	[illegible][a]	[illegible][a]
Btu/lb	5449	5381	5803	[illegible][a]	[illegible][a]
C, wt.%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
S	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cl	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ash	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
O (Difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00	100.00	100.00
Pyrolytic Oil, Dry % of dry feed wt.	16.8	20.1	20.9	18.4	17.2
Gross Heating Value, cal/g	[illegible]	6700	[illegible]	6400	[illegible]
Btu/lb	11,800	12,100	11,100	11,500	[illegible]
C, wt.%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
S	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cl	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ash	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
O (Difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00	100.00	100.00
Pyrolytic Gas, Dry % of dry feed wt.	15.1	16.4	10.5	1.6	9.5
Gross Heating Value, kcal/m³	[illegible]	2750	2130	1170	1520
Btu/scf	[illegible]	[illegible]	[illegible]	[illegible]	163
H_2, mol %	[illegible]	[illegible]	[illegible]	11.51	7.82
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00	100.00	100.00
Pyrolytic Water,[b] % of dry feed wt.	12.2	7.1	10.1	12.5	10.7
Total products, % of dry feed wt.	71.7	80.2	89.5	83.5	81.2

[a] Calculated
[b] Excluding feed moisture

Table 1-3. LABORATORY PYROLYSIS RESULTS - FIR BARK

Run Number	372-26	372-28	372-32	372-42	372-44
Feed Size, mesh	-200	-200	-200	-24	-200
Reactor Exit Temp., °C	510	432	371	510	538
°F	950	810	700	950	1000
Feed Analysis, Wt % dry					
C	49.50	48.30	49.09	52.20	49.03
H	5.56	5.21	5.47	4.21	5.37
N	0.14	0.17	0.19	0.32	0.27
S	0.04	0.03	0.05	0.16	0.09
Cl	0.10	0.20	0.04	0.02	0.01
Ash	8.69	11.72	9.92	5.65	10.72
O (difference)	35.97	34.35	35.24	37.44	34.49
	100.00	100.00	100.00	100.00	100.00
Feed Moisture, Wt %	0.79	1.54	4.20	0.0	2.60
Pyrolytic Char, dry					
% of dry feed wt	27.0	41.0	55.1	39.3	31.7
Gross Heating Value, cal/g	4211	4589	4500^a	5300^a	4400^a
Btu/lb	7579	8260	8100^a	9500^a	8000^a
C, Wt %	40.10	49.86	49.93	50.11	51.32
H	2.38	4.02	3.75	3.34	2.92
N	0.23	0.16	0.17	0.28	0.22
S	0.00	0.09	0.14	0.10	0.07
Cl	0.37	0.17	0.06	0.02	0.03
Ash	33.71	21.30	19.67	13.16	27.42
O (difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00	100.00	100.00
Pyrolytic Oil, dry					
% of dry feed wt	15.5	28.7	20.0	26.7	27.0
Gross Heating Value, cal/g^a	6000	5700	5400	6400	7000
Btu/lb^a	11,000	10,300	9700	11,500	12,700
C, Wt %	62.57	60.45	57.73	62.00	69.12
H	6.84	5.90	6.35	7.05	6.60
N	0.53	1.40	0.20	0.30	0.86
S	0.04	0.07	0.00	0.13	0.00
Cl	0.07	0.10	0.07	0.04	0.02
Ash	0.32	2.00	0.13	0.50	1.21
O (difference)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00	100.00	100.00
Pyrolytic Gas, dry					
% of dry feed wt	14.2	8.2	6.1	5.7	27.0
Gross Heating Value, kcal/scm	3620	3000	4800	2700	1610
Btu/scf	406	337	510	287	171
H_2, Mol %	16.00	0.20	52.37	1.80	2.38
[illegible]	14.43	14.80	22.71	28.84	26.32
[illegible]	30.23	64.70	52.19	49.65	63.80
[illegible]	15.25	10.40	6.17	7.00	2.53
[illegible]	3.69	1.03	1.40	1.57	0.83
[illegible]	1.05	0.37	14.30	0.13	0.23
[illegible]	1.05	0.86	0.71	0.79	0.44
[illegible]	1.65	0.00	0.31	1.42	0.83
[illegible]	11.58	1.08	0.20	1.42	1.13
	100.00	100.00	100.00	100.00	100.00
Pyrolytic Water^b, % of dry feed wt	1.9	15.2	9.2	14.0	15.0
Total Products, % of dry feed wt	17.4	93.7	97.0	86.1	121.1

^{a} Calculated

^{b} Excludes feed moisture

Table [illegible]. LABORATORY PYROLYSIS RESULTS - [illegible]

Run Number	[illegible]	[illegible]	[illegible]
Feed Size, mesh	[illegible]	[illegible]	[illegible]
Reactor Wall Temp., °C	[illegible]	[illegible]	[illegible]
°F	[illegible]	[illegible]	1000
Feed Analysis, Wt % dry			
C	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]
S	[illegible]	[illegible]	[illegible]
Cl	[illegible]	[illegible]	[illegible]
Ash	[illegible]	[illegible]	[illegible]
O (difference)	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00
Feed Moisture, Wt %	0.0	1.30	1.44
Pyrolytic Char, dry			
% of dry feed wt	[illegible]	[illegible]	[illegible]
Gross Heating Value, cal/g[a]	[illegible]	[illegible]	[illegible]
Btu/lb[a]	[illegible]	[illegible]	[illegible]
C, Wt %	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]
S	[illegible]	[illegible]	[illegible]
Cl	[illegible]	[illegible]	[illegible]
Ash	[illegible]	[illegible]	[illegible]
O (difference)	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00
Pyrolytic Oil, dry			
% of dry feed wt	[illegible]	[illegible]	[illegible]
Gross Heating Value, cal/g[a]	[illegible]	[illegible]	[illegible]
Btu/lb[a]	[illegible]	[illegible]	10,000
C, Wt %	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	[illegible]
S	[illegible]	[illegible]	[illegible]
Cl	[illegible]	[illegible]	[illegible]
Ash	[illegible]	[illegible]	[illegible]
O (difference)	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00
Pyrolytic Gas, dry			
% of dry feed wt	[illegible]	[illegible]	[illegible]
Gross Heating Value, kcal/m³[a]	[illegible]	[illegible]	[illegible]
Btu/ft³[a]	[illegible]	[illegible]	[illegible]
H_2, Mol %	[illegible]	[illegible]	[illegible]
CO	[illegible]	[illegible]	[illegible]
CO_2	[illegible]	[illegible]	[illegible]
CH_4	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	100.00	100.00	100.00
Pyrolytic Water[b], % of dry feed wt	[illegible]	[illegible]	[illegible]
Total Products, % of dry feed wt	[illegible]	[illegible]	[illegible]

[a] Calculated

[b] Excluding feed moisture

The composition of the dry char reported in Tables I-1 through I-4 is the mass average of the compositions of the dry-basis chars removed from the three cyclones. For example,

$$\text{Per cent carbon dry basis} = \frac{\Sigma\,\text{Wt carbon from each cyclone}}{\Sigma\,\text{Total dry wt from each cyclone}} \times 100\%$$

Oil -

The major part of the pyrolytic oil in each run was recovered from the glass condenser train and the five micron filter bag. As much product as possible was recovered by decanting from the various vessels, and the total amount of material was determined by weighing the decanted portions and weighing each piece of the glass train both before and after the run. The decanted portions were submitted for analysis, and their moisture contents and quinoline-insoluble contents were subtracted to determine the amount of dry, char-free pyrolytic oil collected from each section of the glass collection train and the filter bag. In addition, the amount of aerosol oil product was calculated from the weight of aerosol caught on the Pall filter and the Gelman filter in the H_2O/H_2S sampling train, and the measured volume of the portion of reactor off gas passing through the H_2O/H_2S train. The total oil yield was calculated as follows:

$$\text{Dry oil yield} = \frac{\begin{array}{c}\text{Wt oil in glass vessels, dry, char-free +}\\ \left(\text{Wt oil in filter bag, dry, char-free +}\right)\\ \text{Wt aerosol oil calculated, dry basis}\end{array}}{\text{Wt feed, dry basis}} \times 100\%$$

The composition of the dry pyrolytic oil reported in Tables I-1 through I-4 is the mass average of the compositions of the dry-basis material decanted from the three collection flasks in the glass condenser train. The implicit assumption that this mass average composition is representative of all the pyrolytic oil, including the undecanted residue, the filter bag catch, and the aerosol, is believed to be quite accurate.

Gas -

The composition of the pyrolytic product gas from each run shown in Tables I-1 through I-4 was determined as follows. For each component (H_2, CO, etc.) the ratio (moles component/moles carrier gas) was calculated from the analyses of both gas samples and the results averaged. From these average component ratios, as well as from the weight of H_2S caught by the $CuSO_4$/Drierite trap in the H_2O/H_2S sampling train, the carrier-gas-free pyrolytic gas composition was determined. The pyrolytic gas yield was then calculated from the composition and the measured volume of carrier gas used during the run.

In spite of the improvements made to the gas sampling train during the program, a number of factors adversely affect the reliability of the reported gas yields and compositions.

1. The low feed rate sometimes obtained with the vibrating screw feeder caused the gas sample to be over 99% carrier gas in some cases. This made an accurate gas analysis difficult.

2. The concentrations of CO_2 and H_2 varied from run to run in a way apparently unrelated to temperature or other operating conditions. These variations can be seen in Tables I-1 through I-4. However, this problem may be due to the mass spectrometry/gas chromatography analytical technique, since frequent inconsistencies were noted between H_2 and CO_2 concentrations in the two gas samples collected from the same run.

Since the gas yield is calculated on the basis of the gas composition, whatever unreliability is attached to the composition extends to the yield also.

Water -

Even though pyrolysis occurs in the absence of oxygen in the Garrett process, a significant amount of water is produced due to the fairly high oxygen content in the feed materials. In the bench scale pyrolysis tests, part of the pyrolytic water was recovered from the glass condenser train and the five micron filter bag, as moisture in the oil and occasionally as a separate aqueous phase. The additional water produced was calculated from the weight gain in the Drierite traps and the measured volume of reactor gas passed through the H_2O/H_2S train. The moisture content of the recovered char also added a small amount to the water yield. The total water yield was calculated as follows:

$$\text{"Dry" water yield} = \frac{\left(\begin{array}{l}\text{Wt moisture in cyclones} + \\ \text{Wt moisture in glass vessels and filter} + \\ \text{Wt moisture calculated from trap} - \\ \text{Wt moisture in feed}\end{array}\right)}{\text{Wt feed, dry basis}} \times 100\%$$

While pyrolytic water and oil are collected together in the laboratory equipment, they will be collected separately in the pilot plant using procedures similar to those envisioned for a commercial plant. However, based on past experience on pyrolysis of municipal solid waste, the separated pyrolytic water is still expected to retain a fairly high concentration of organics which, while completely biodegradable, could cause a secondary pollution problem. In the design of a commercial plant, therefore, careful attention must be given to reducing such pollution to a minimum.

Product Heating Values

Gross heating values, or higher heats of combustion, for the pyrolytic oils and chars are reported in Tables I-1 through I-4. Some of the char heating values were determined by an outside testing laboratory, but all others were calculated from the empirical Dulong-Berthelot correlation:

$$\text{cal/g} = 81.37(\%C) + 345(\%H - \frac{\%N + \%O - 1}{8}) + 22.2(\%S)$$

Empirical correlations of this type were originally developed for coal-like fuels. However, this correlation does provide a good approximation for the heating values of these solid waste chars, as indicated by comparing bomb calorimeter values with calculated results shown in Table I-5. The Dulong correlation is known to be valid for pyrolytic liquid fuels also, as evidenced by calorimeter data obtained from earlier Garrett studies on municipal solid waste.

Table I-5. COMPARISON OF EXPERIMENTAL VS. CALCULATED CHAR HEATING VALUES

Run Number	Bomb Calorimeter Results, cal/g	Dulong-Berthelot Calculated Results, cal/g
372-22	3027	3200
372-24	2990	3100
372-26	4211	4100
372-28	3324	3600
372-30	4589	4400

Material Balance

The raw product yields reported in Tables I-1 through I-4 do not always add up to 100%. However, the conversions of dry feed to products must be made to total 100% in some reasonable way in order to draw rational conclusions from the laboratory data. The manner in which these "correct" product yields were determined is summarized below.

The material and elemental balances implicit in the formation in Tables I-1 through I-4 can be regarded as a system of linear equations. In order to choose which quantities should be unknowns and which information (equations) should be used to solve for these unknowns, the following guidelines were observed.

1. A high degree of reliance can be put on the reported pyrolytic char yield, since the recovery of this product is quite straightforward, i.e. weighing the material.

2. A fairly high degree of reliance can be put on the reported ultimate analyses of the feed and the pyrolytic char.

3. The reported gas composition should not be relied upon too heavily due to known sampling variations.

4. The reported pyrolytic oil, gas, and water yields should not be heavily relied on.

For each pyrolysis run, two calculations were made (by a simple computer program).

1. The four product yields -- per cent char, oil, gas and water -- were considered unknown, and the four linear equations used to solve for them were:

    a) Total products = total feed
    b) Ash in char and oil = ash in feed
    c) Carbon in char, oil and gas = carbon in feed
    d) Hydrogen in all four products = hydrogen in feed

2. The reported per cent char yield was accepted as known, and the other three product yields were considered unknown. The three equations used to solve for them were the overall, carbon and hydrogen balances, i.e. (a), (c), and (d) above.

In 17 cases (out of 21 runs) the char yield calculated by the first procedure agreed closely with the yield reported in Tables I-1 through I-4. In these cases the calculation by the second procedure was adopted, i.e. the reported char yield was accepted as being accurate, and only the oil, gas and water yields were calculated. In four cases the char yield calculated by the first procedure was significantly different (by up to 17% yield) from the reported char yield, and in these cases, the calculation from the first procedure was adopted.

Several spot checks were made on the sensitivity of the calculation procedures to variations in input data, and the following observations are noted.

1. Variations in the reported ash, carbon and hydrogen contents of the feed had a significant effect on all calculated yields. This is disturbing because ultimate analyses of thw feed materials occasionally did show unexpected changes, due perhaps to failure to obtain a representative sample for analysis.

2. Variation of the ash content in the pyrolytic oil had a negligible effect on the calculated product yields.

3. Variation of the CO/H_2 levels in the pyrolytic gas composition had a negligible effect on the calculated product yields.

All subsequent interpretation in this report of the results of the laboratory pyrolysis phase is based on the "corrected" yields of pyrolytic char, oil, gas and water determined by the procedures discussed above. The justification for this is as follows:

1. Meaningful interpretation and comparison of yield results cannot be made if yields do not total 100%.

2. The procedure used to determine the "corrected" yields is simple and a minimum of subjective judgment was involved.

3. In most cases, the pyrolytic oil yield was the only value substantially changed from the raw data yield. The implication is that the "adjustments" are thus not artificial, but are corrections for experimental limitations in the product collection system and/or procedure.

INTERPRETATION OF RESULTS

Rice Hulls

Yields of dry pyrolytic char, oil, gas and pyrolytic water are shown in Figure I-1. The char yield clearly decreases as the pyrolysis temperatures are increased. However, the oil yield of about 40% is apparently independent of pyrolysis temperature over the range investigated.

The effect of increased feed particle size is seen in the char yields plotted at 421 and 504°C. These two runs were made with minus 20 mesh feed rather than the minus 200 mesh used for the other six runs. The two char yields are higher than would be expected from the trend with temperature, implying that the larger particles are not completely pyrolysed in the short residence time provided in the bench scale reactor. However, the oil yield at 504°C was apparently not adversely affected by the larger particle size.

The effect of feed moisture content is seen in several of the rice hull runs. The runs conducted at 510 and 521°C were made with feed containing over 3% moisture, and the respective char yields are high compared to the observed trend with respect to temperature. The runs at 427, 504 and 518°C were made with feed containing only around 2.5% moisture, and the char yields of the latter two also seem high. On the other hand, moisture content does not appear to have much effect on oil yields. A reasonable explanation of the effect of feed moisture is that additional residence time is required in order to achieve a given extent of pyrolysis, much as larger feed particles require additional time.

One of the economic attractions of flash pyrolysis is the high conversion to volatile products which is obtainable compared to longer residence time processes. In fact, numerous studies are reported in the literature (e.g. Badzioch and Hawksley) where the dry weight lost during flash pyrolysis of coal is often greater than the volatile content as determined by ASTM test methods. It is of interest, therefore, to see what happens to the moisture and ash free portion of the industrial wastes investigated during flash pyrolysis. Figure I-2 shows the volatile components in the feed and in the products from pyrolysis of rice hulls. Each pyrolysis run is represented by a group of three columns. The first column shows the per cent of the moisture and ash free rice hulls feed which reports as gas and as tar plus light oil, by a Fischer assay to 500°C.

FIGURE 2-1. Product yields vs. temperature

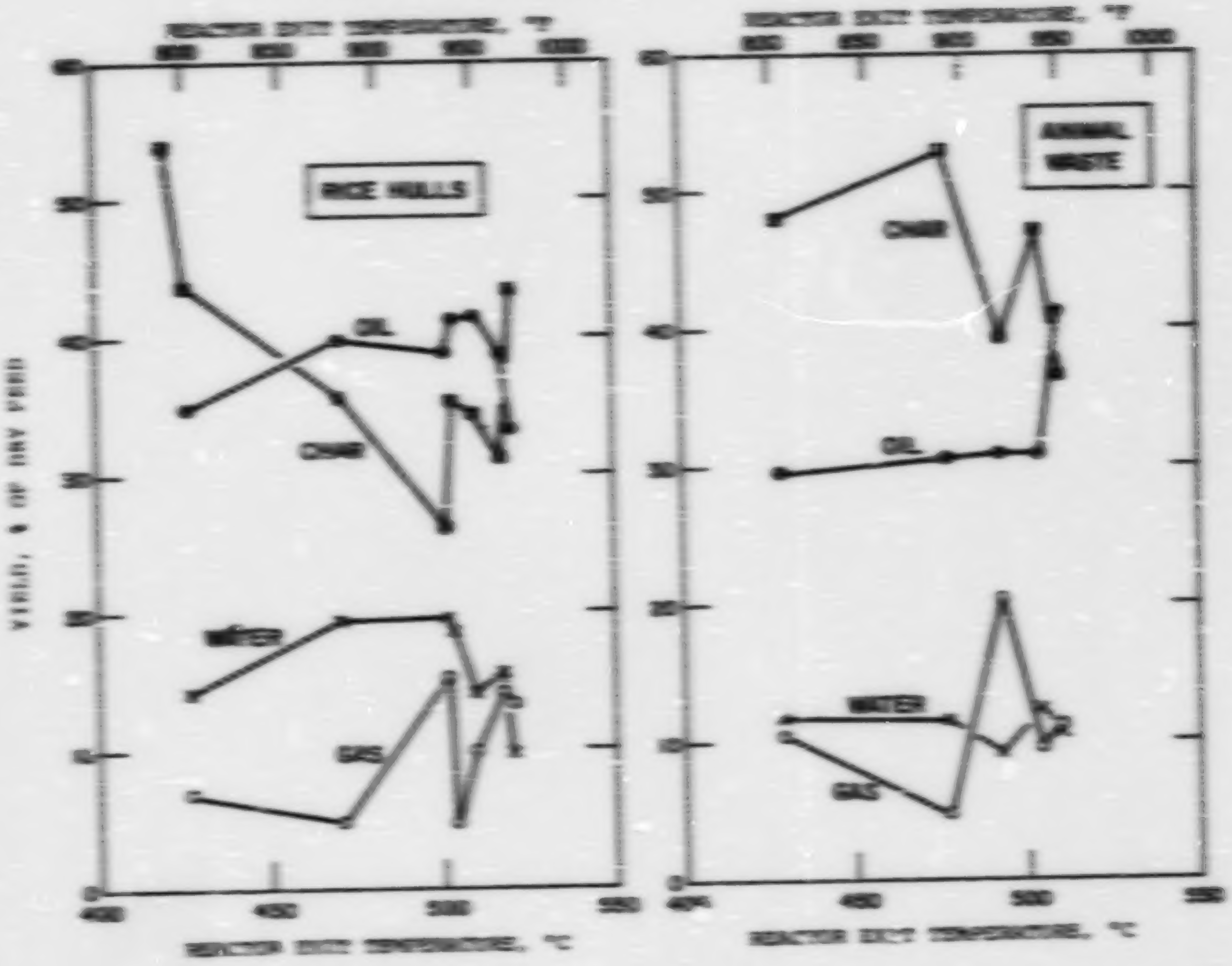
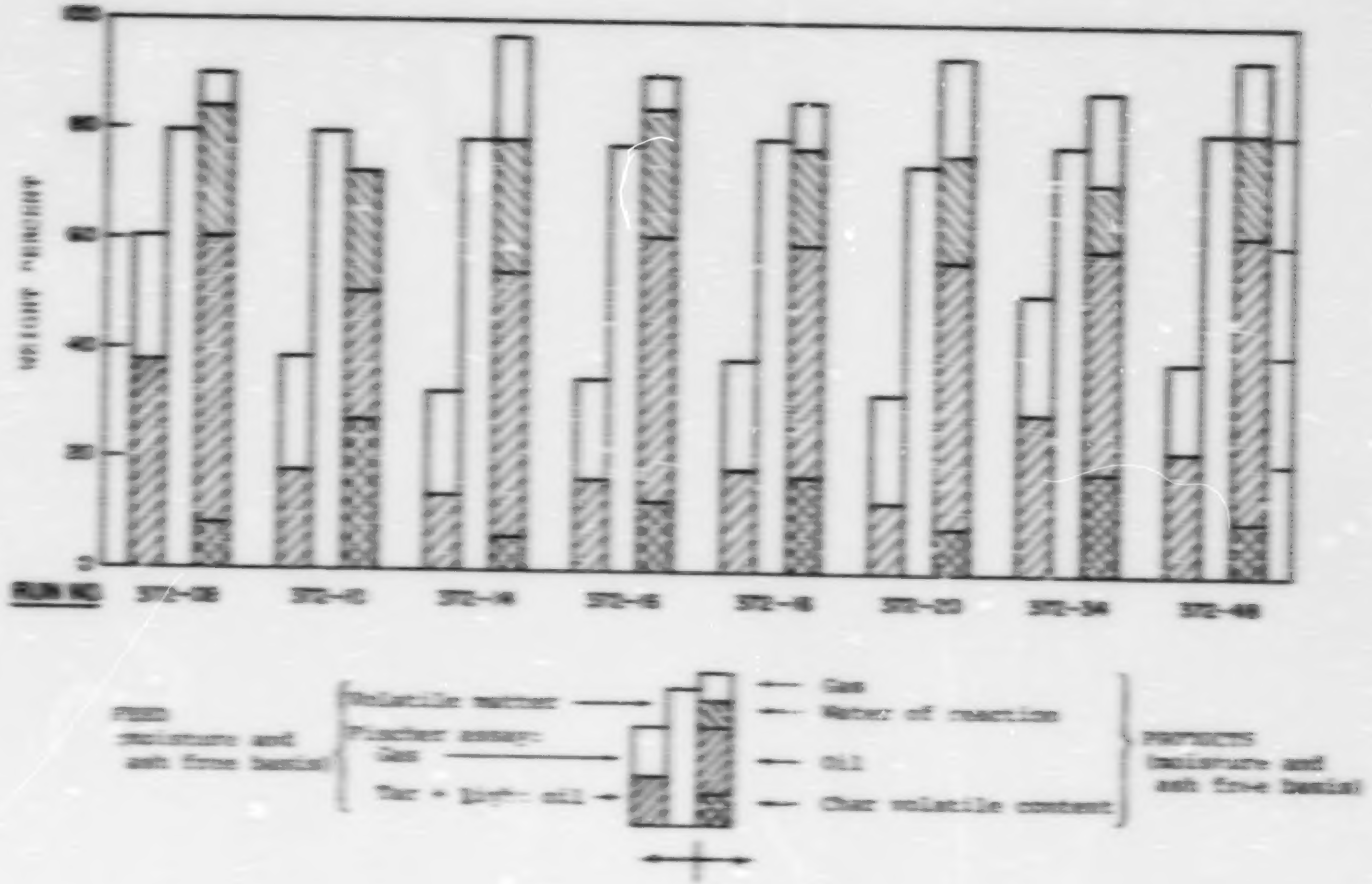


FIGURE 3-2. Distribution of volatiles in feed and products: Rice hulls



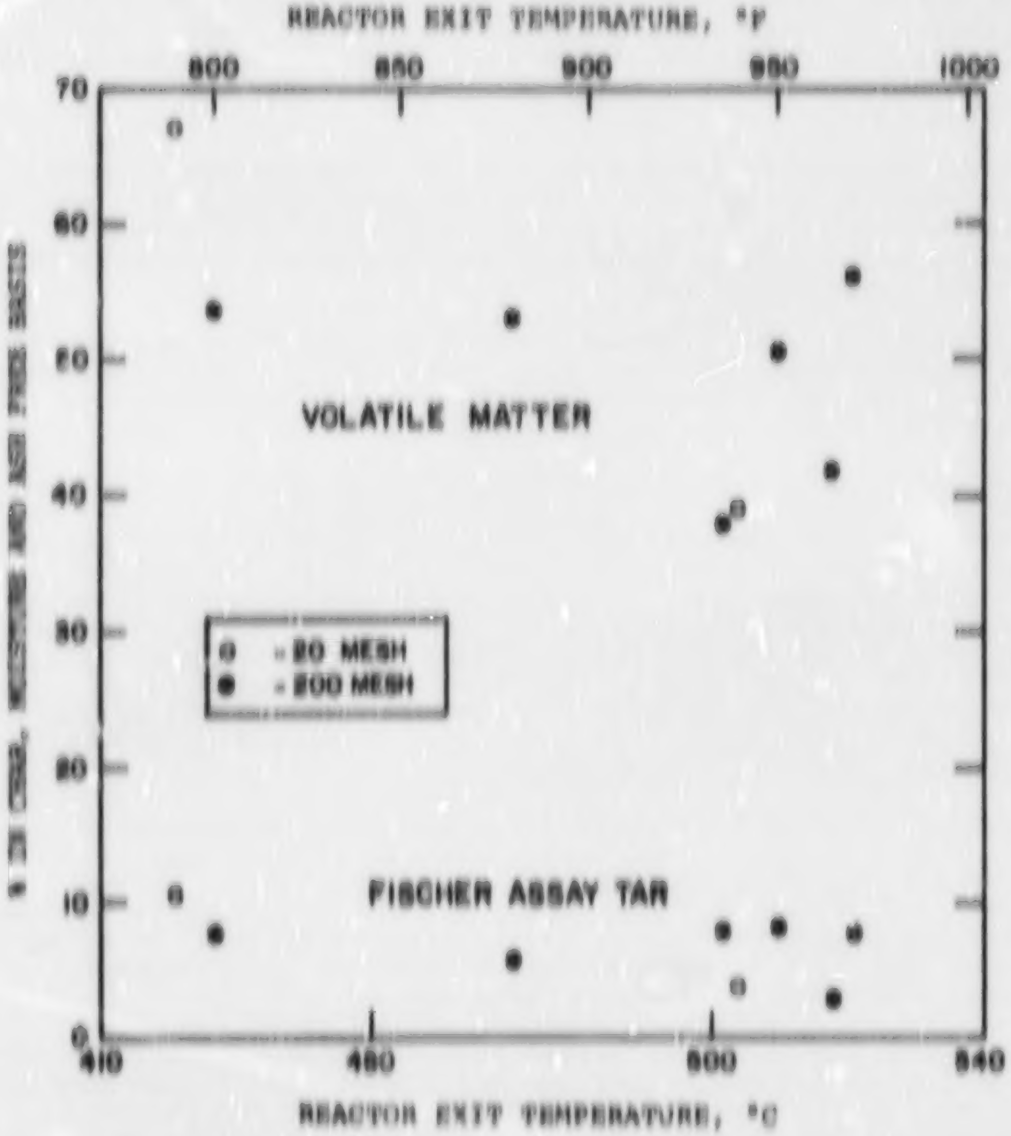
Qualitatively, this column indicates the gas and oil yields which could be obtained by long residence time pyrolysis. The second column shows the per cent volatile matter in the moisture and ash free feed. This represents the potential yield (mostly gas) at 950°C for an "infinite" residence time. The third column shows the pyrolytic oil, water and gas yields from Figure I-1 as well as the volatile matter remaining in the pyrolytic char. All four quantities are expressed as a per cent of the feed on a moisture and ash free basis. This third column represents the total volatile matter recovered from flash pyrolysis.

Comparison of the heights of the second and third columns of each group demonstrates the advantage of flash pyrolysis over long residence time operations. In every case (except run 372-10 for which no gas analysis was made) the total volatile content of the products exceeds the volatile matter of the feed. Furthermore, in many cases the weight loss from the feed (gas, water and oil yields, third column) is greater than the volatile matter in the feed. This means that during flash pyrolysis operations there occurs a substantial amount of gasification of the fixed carbon in the feed. This result is of great economic significance, since it demonstrates that the advantage of flash pyrolysis over long residence time processing, previously documented for coal conversion, can be exploited for the conversion of industrial wastes as well.

It is also useful to compare the first column, Fischer assay tar, light oil and gas, with the pyrolytic oil and gas yield portions of the third column. In almost every case the yield of usable synthetic fuels from flash pyrolysis is greater than the Fischer assay tar, light oil and gas of the feed material.

The quality of the pyrolytic char from rice hulls is indicated in Figure I-3. The presumption is that the more completely the char has been devolatilized, the higher its potential value for upgrading to an activated charcoal substitute. Per cent volatile matter remaining in the char is plotted versus temperature, and per cent Fischer assay tar is also shown for comparison and for qualitative confirmation of trends observed in the volatile matter content. The expected temperature effect is observed, that is, at higher pyrolysis temperature the product char has been more completely devolatilized. The volatile matter contents correlate strongly with the char yields shown in Figure I-1, suggesting that temperature, particle size and feed moisture content all have qualitatively the same effects on extent of devolatilization as they do on char yield. This is reasonable, of course.

FIGURE I-3. Char devolatilization vs. temperature: Rice hulls



Since rice hulls have a relatively high ash content, the product char is commensurately high in ash. The properties of this ash could have an important effect upon the design of a full scale pyrolysis plant. Fusion tests on the ash from the pyrolytic char showed its softening temperature to be about 1500°C (2700°F) in an oxidizing or reducing atmosphere. Such a high temperature will not be approached in any commercial plant, but the abrasion characteristics of the ash may have to be considered. The ash in rice hulls consists of approximately 35% silicon and 11% sodium and potassium as determined by emission spectrographic analysis.

Animal Waste

Yields of dry pyrolytic char, oil, gas and pyrolytic water are shown in Figure I-1. Again the char yield clearly decreases with increased pyrolysis temperature while the oil yield, at about 30%, appears to be independent of temperature in the range investigated.

The effect of feed moisture content on char yield appears to be quite strong. The two highest char yields, from the runs at 477 and 504°C, correspond to the highest feed moisture contents, which, however, were both less than 3%.

The distribution of volatiles in the feed and products from these runs is shown in Figure I-4. Again the total volatile content in the products (third column) exceeds the volatile matter of the feed (second column). However, in contrast to rice hull pyrolysis, the amount of usable devolatilization products, i.e. the pyrolytic oil and gas in the third column, is equal to or only slightly greater than the Fischer assay tar, light oil and gas in the first column. Also to be noted are the high ash and nitrogen contents of the pyrolytic oil from animal waste (see Table I-2), compared to the oil from the other feed materials.

Devolatilization of the pyrolytic char from animal waste is shown in Figure I-5. Here again the volatile matter remaining in the pyrolytic char correlates well with the char yield shown in Figure I-1. The one exception is the low volatile matter plotted at 477°C; this is believed to be an error in analysis, particularly in view of the relatively high Fisher assay tar in the same char.

The pyrolytic char from animal feedlot wastes was quite high in ash content. This ash had a softening temperature of about 1200°C (2200°F), which would not be expected to cause problems in the full scale process. However, the animal waste ash contained about 28% sodium and potassium, and such a high concentration of water soluble constituents destroys the char's potential as an activated carbon substitute for water treatment applications.

FIGURE 3-4. Distribution of volatiles in feed and products: Animal waste

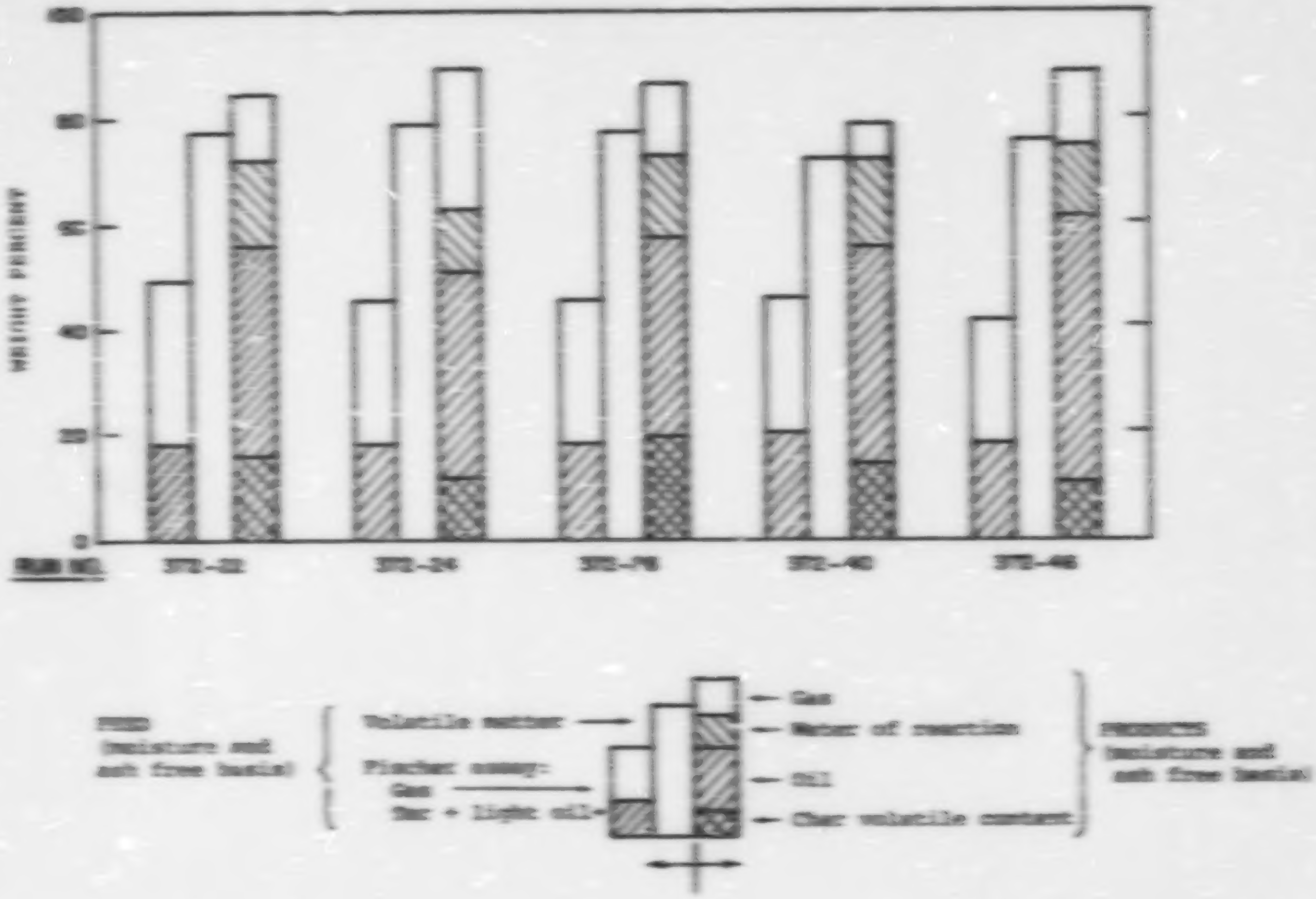
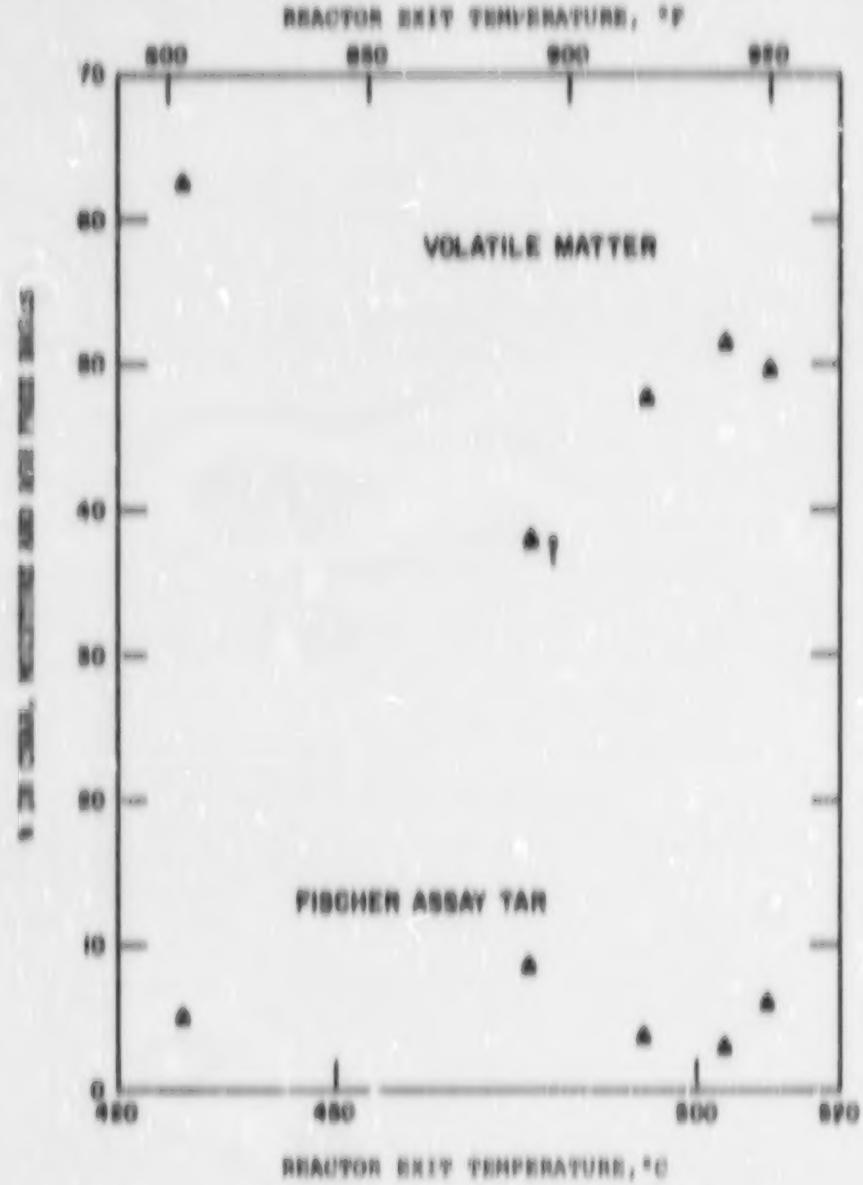


FIGURE 5-5. Char devolatilization vs. temperature: Animal waste



Fir Bark

Yields of dry pyrolytic char, oil, gas and pyrolytic water from Douglas fir bark are shown in Figure I-6. The char yield appears to decrease generally with increasing pyrolysis temperature, as is reasonable. The oil yield improves with increasing pyrolysis temperature. The effect of minus 24 mesh feed rather than minus 200 mesh is consistent with the results discussed earlier for rice hulls. The char yield from 372-42 (minus 24 mesh) at 510°C is much higher (39%) than from run 372-26 (minus 200 mesh) at the same temperature. Correspondingly, the oil yield is much lower (28%) from the larger particle size feed. Moisture content of the feed has the same effect on char yield as noted previously. The two runs showing relatively high char yields in Figure I-6, at 471 and 538°C, correspond to the highest feed moisture contents, although both were less than 5% moisture. In the bark pyrolysis runs, however, in contrast to rice hulls and animal waste, the oil yield also was affected by feed moisture, in just the opposite way from the char yield; that is, moisture in the fir bark feed had a detrimental effect on the pyrolytic oil yield.

The moisture and ash free volatile components in bark and its pyrolysis products are shown in Figure I-7. The amount of usable devolatilization products, indicated by the pyrolytic gas and oil parts of the third column in each set, is substantially greater than the Fischer assay tar, light oil and gas shown in the first column of each set, for the higher temperature runs (372-26, 372-42, 372-44). For the other two runs the total yield of devolatilization products from flash pyrolysis is about the same as the Fischer assay tar, light oil and gas. In all cases the total volatile content of the products is greater than the volatile matter in the feed.

The extent of char devolatilization is shown in Figure I-8. The volatile matter content remaining in the pyrolytic char correlates closely with the char yields shown in Figure I-6, even including the effect of the larger minus 24 mesh particle size run at 510°C. The Fischer assay tar contents are consistent with the volatile matter analyses. The ash content of the pyrolytic char from fir bark was relatively low and the ash had a softening temperature of about 1200°C (2200°F). Emission spectrographic analysis of the tree bark ash showed only about 9% sodium and potassium.

Grass Straw

The yields of dry pyrolytic char, oil, gas and pyrolytic water on a dry feed basis are shown in Figure I-6. In the grass straw pyrolysis runs, only minus 200 mesh feed was

FIGURE 3-4. Product yields vs. temperature

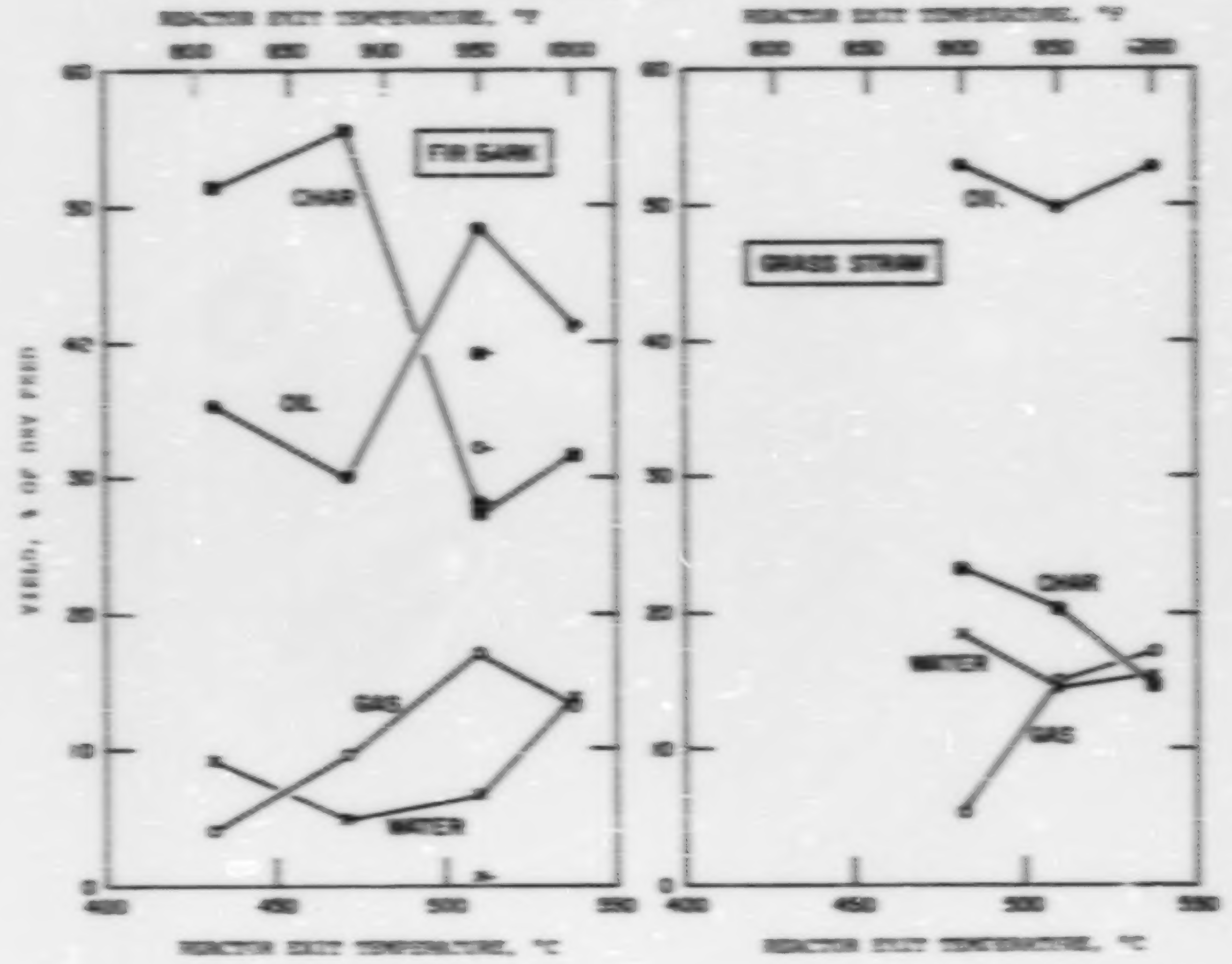


FIGURE 3-7. Distribution of volatiles in feed and products: Fir bark

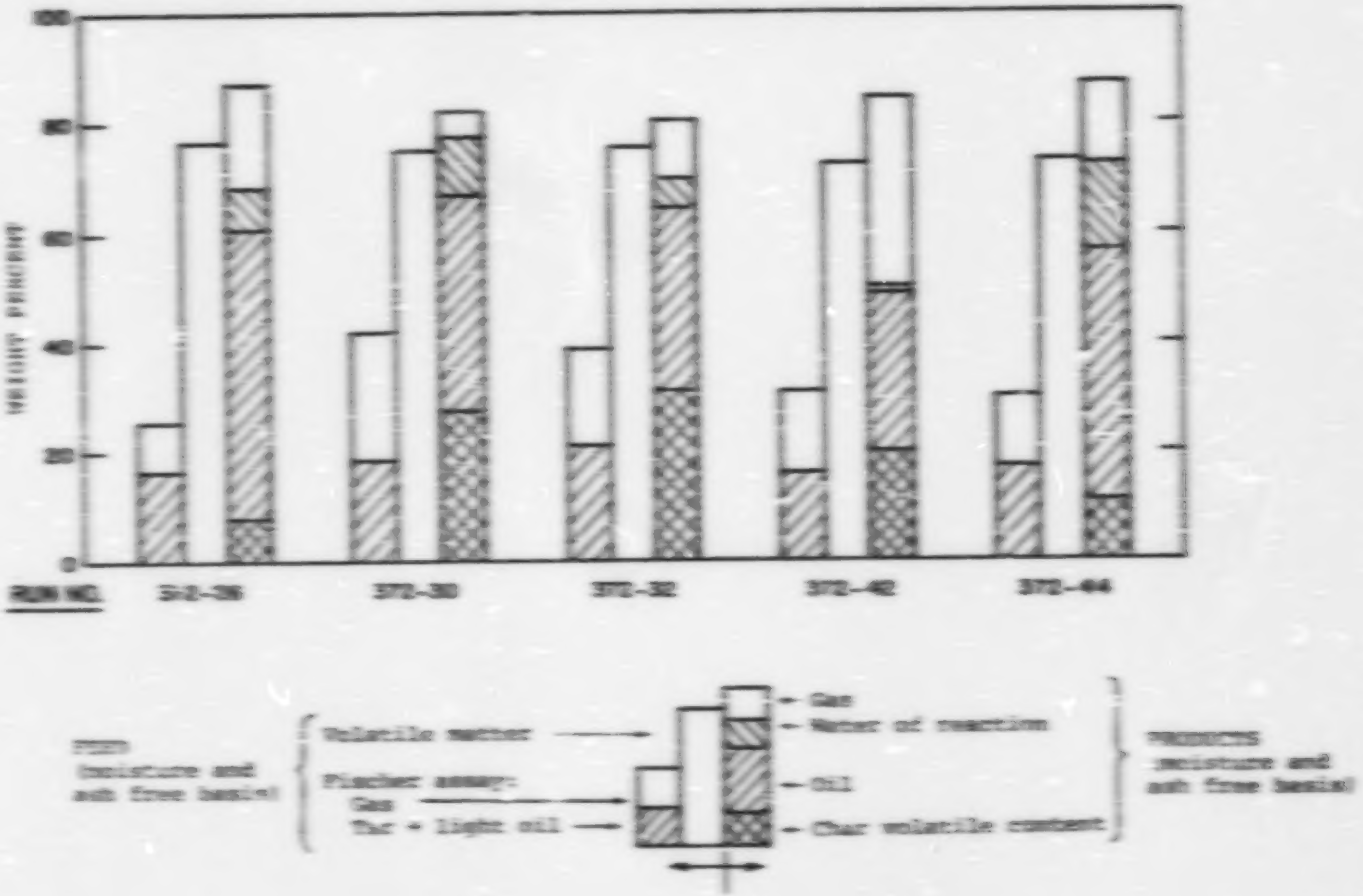
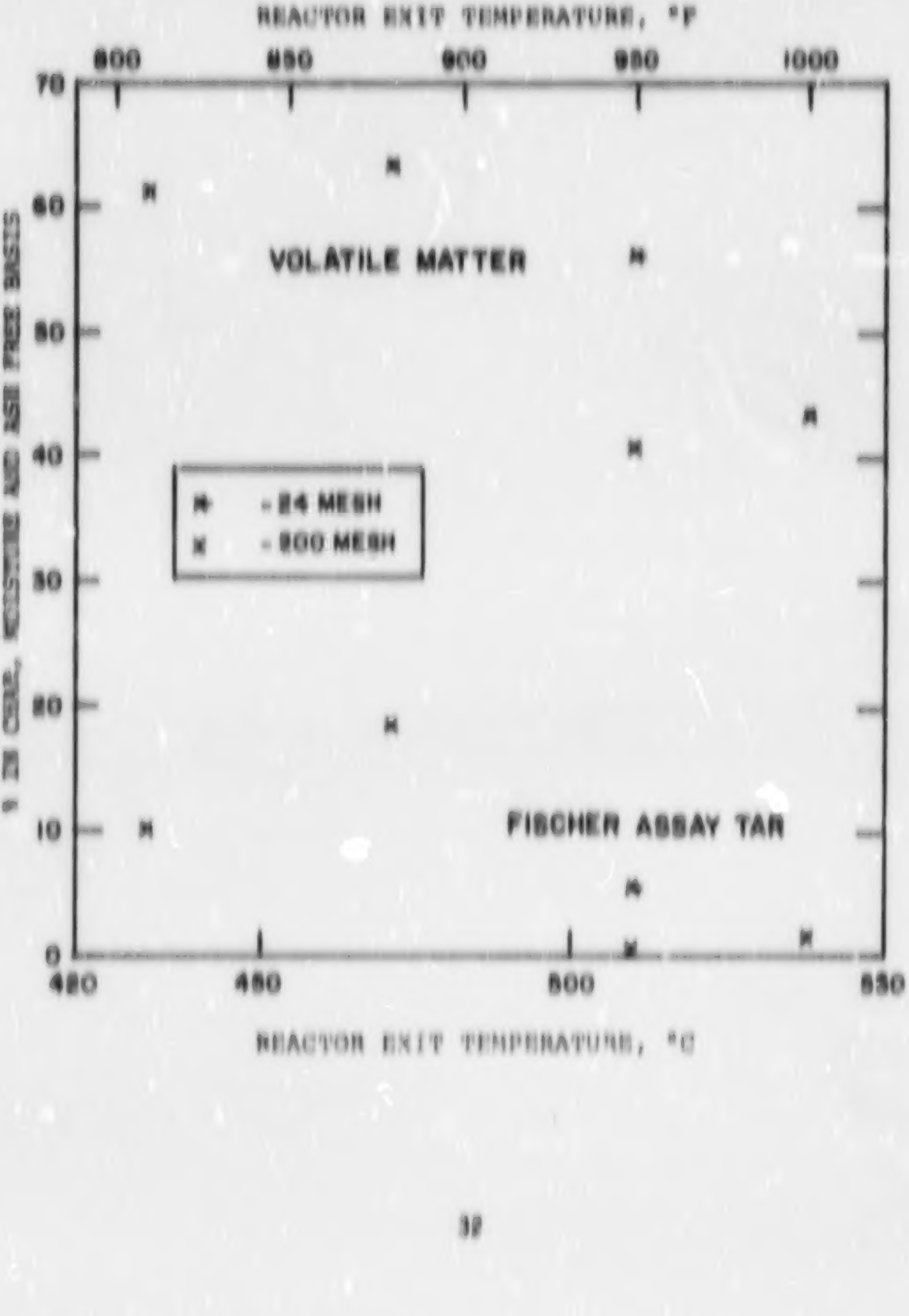


FIGURE I-6. Char devolatilization vs. temperature: Fir bark



used, and its moisture content was always less than 1.5%; so the only variable was pyrolysis temperature.

The yield of dry pyrolytic char is very low compared to the yield from the other three feed materials. It decreases with increasing pyrolysis temperature. The oil yield is consistently 50% or more, and does not appear to be much affected by the pyrolysis temperature over the 60°C range investigated.

Pyrolysis of the moisture and ash free volatile portion of the grass straw is illustrated in Figure I-9. Comparison of the pyrolytic gas and oil in the third column of each set with the Fischer assay tar, light oil and gas in the first column illustrates dramatically that grass straw is a high grade feedstock for flash pyrolysis. It is also notable that pyrolytic oil accounts for most of the volatile product. As with the other feedstocks, the total volatile content of the products exceeds the volatile matter in the grass straw feed. Even further, the feed weight loss (gas, oil and water in the third column) is greater than the volatile content of the feed, in all three runs.

The quality of the devolatilized pyrolytic char is shown in Figure I-10. The effect of temperature on volatile matter remaining in the char is very similar to its effect on char yield. (The inconsistently high Fischer assay tar of almost 6% at a pyrolysis temperature of 510°C may be incorrect.)

Comparison of Pyrolytic Oil Yields from All Feedstocks

The yields of pyrolytic oil versus temperature for all four feed materials studied are summarized in Figure I-11. The left-hand plot shows the same oil yields given in Figures I-1 and I-6. In general, grass straw yielded 50% oil, rice hulls and fir bark gave 40%, and animal waste 30%. (The differences among the four materials are largely due to their different ash contents; almost all of the ash goes to pyrolytic char.) It is apparent from this plot especially, that fir bark is the only feedstock of the four for which the yield of pyrolytic oil can be greatly affected by moderate variation in pyrolysis temperature, feed particle size, feed moisture content or (by hypothesis) residence time.

For purposes of economic evaluation, the important oil yield to consider will be the total heating value obtained in the form of oil, from a given weight of feed. This comparison is shown in the right-hand plot of Figure I-11, which was obtained from the oil yields in the left-handplot and the heating values tabulated in Tables I-1 through I-4. Generally,

FIGURE I-9. Distribution of volatiles in feed and products: Grass straw

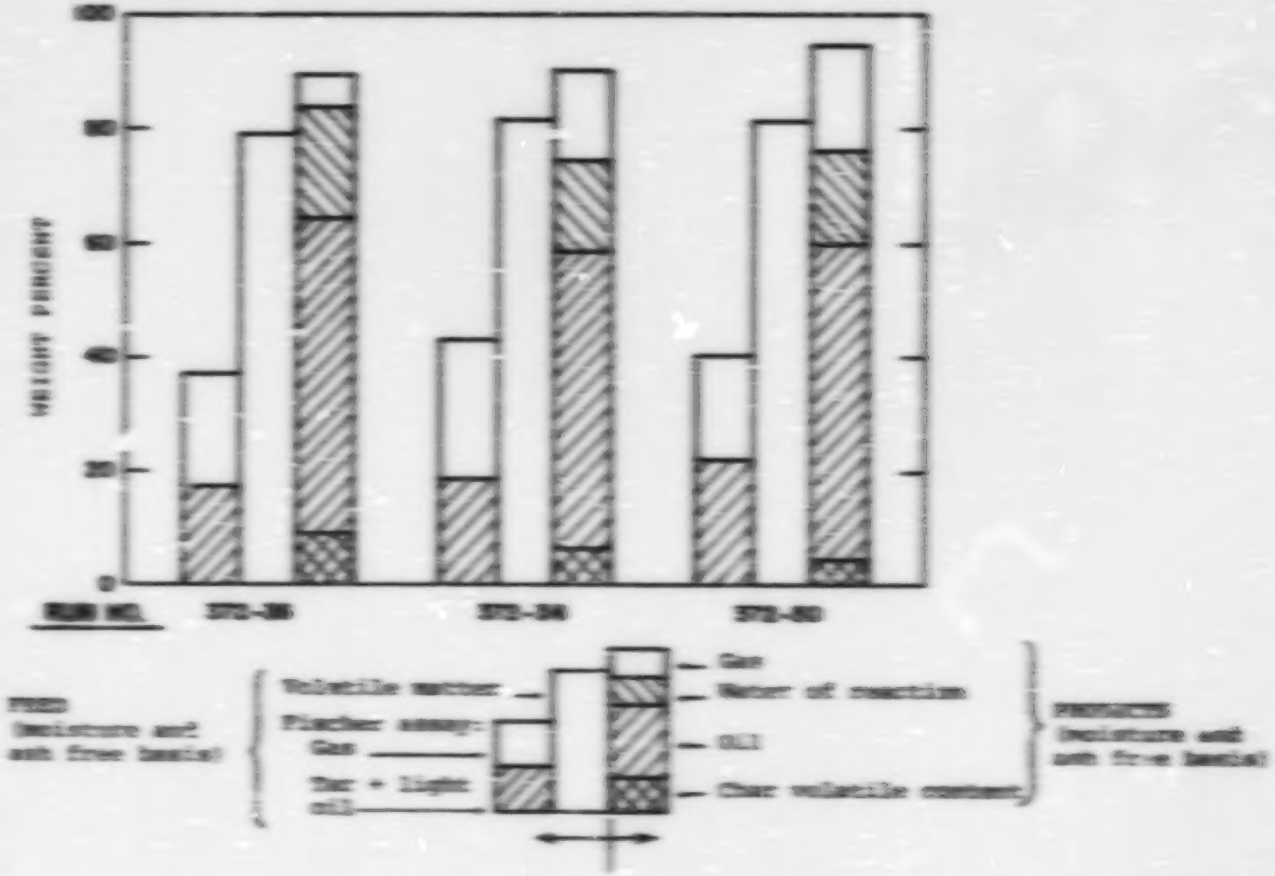


FIGURE I-10. Char devolatilization vs. temperature: Grass straw

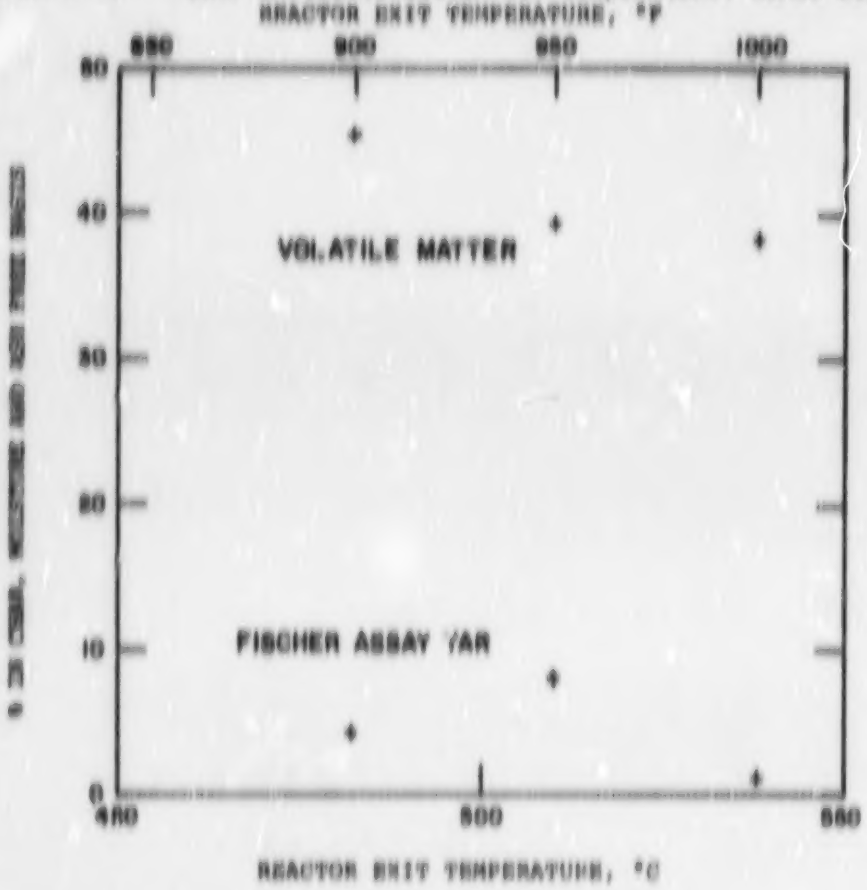
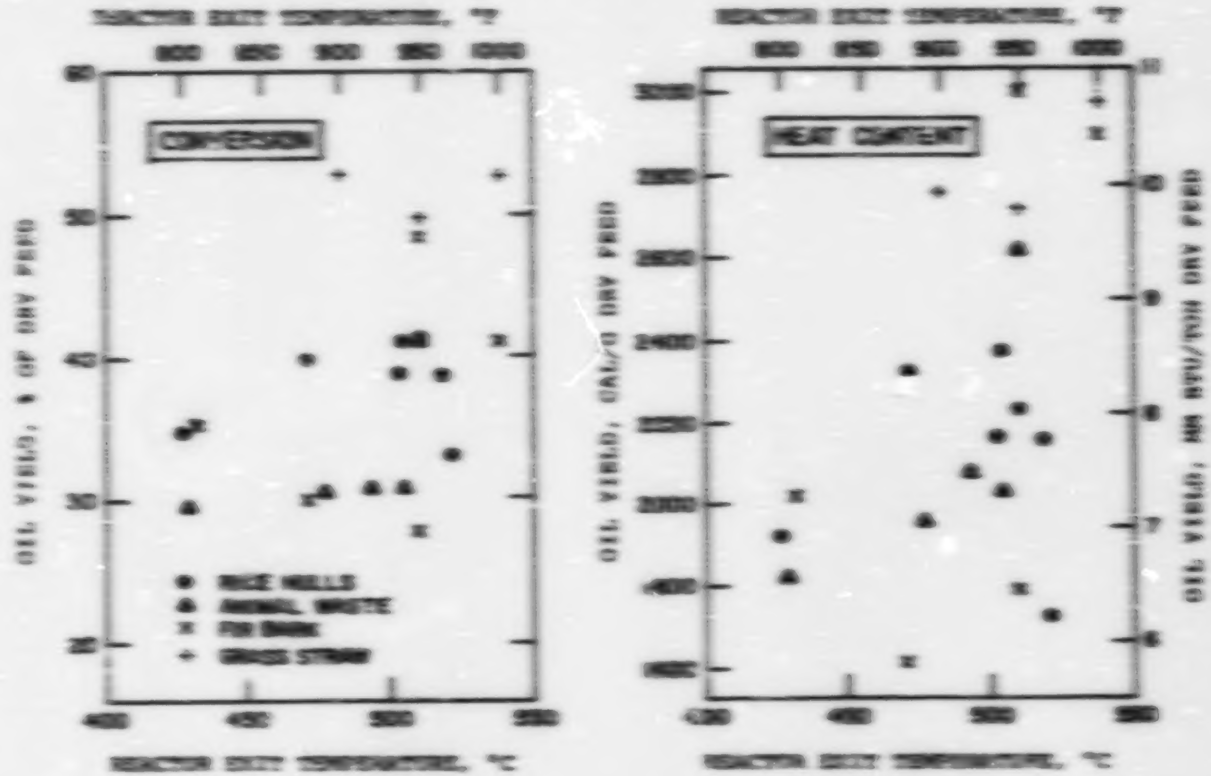


FIGURE 3-11. Pyrolytic oil yields from various feedstocks vs. temperature



this plot confirms the impression to be gained from the left-hand plot. Grass straw gives the greatest heating value in the form of pyrolytic oil. It is confirmed that variations in temperature, particle size and moisture content can drastically affect the oil yields from fir bark, perhaps even so as to exceed yields from grass straw in terms of heating value recovered.

The quality of the pyrolytic oil is not defined by its heating value alone. For example, oil from any of the four feedstocks has a low sulfur content, an advantage in considering the oil as a boiler fuel. However, the nitrogen contents of the oil from animal waste were in the range 5 to 7%. This means the animal waste would require pretreatment before pyrolysis in order to produce a marketable pyrolytic fuel.

Comparison of Pyrolytic Char Yields from All Feedstocks

In consideration of the objective of obtaining activated char from waste materials, it is important to note that over 80% of the volatile material was removed from the feed during most of the bench scale tests. This can be seen by reviewing Figure I-2, I-4, I-7 and I-9. In these figures the double cross-hatched segment of each third column represents volatile matter remaining in the char, while the second column represents the volatile matter in the feed. In most cases the char volatile matter is less than 20% of the original (feed) volatile matter. Exceptions occurred in runs where the pyrolysis temperature was low, or the feed moisture content was high, or a larger feed particle size was used. In a commercial plant using the proprietary Garrett flash pyrolysis process, an even greater degree of devolatilization can be expected, since the char undergoes partial combustion (to supply process heat) before its removal as a product.

SECTION V

PHASE II - PILOT PLANT STUDIES

INTRODUCTION

This section presents the results of the Phase II studies (pilot plant runs) on feed stocks of Douglas fir bark, rice hulls and rye grass straw. The primary objective was to obtain process engineering data to design commercial scale demonstration plants for the flash pyrolysis of these industrial wastes. Yields were obtained by overall, total run, material balances and confirmed by spot stream samples and flow rates when the system had reached steady state. During the pilot plant studies, sufficient quantities of the pyrolysis products (char, oil, and gas) were obtained for characterization and evaluation during Phase III (Product Evaluation) of this program.

The Phase II studies included (1) preparation of feedstock for flash pyrolysis; (2) production of start-up char by direct electrical heating from the reactor walls; (3) production of oil and char for product evaluation; (4) confirmation of operating conditions for optimum yields; and (5) determination of product char properties. The most important parameter, pyrolysis temperature, was established during the Phase I laboratory studies. Based on these data, the expected optimum temperature was selected for all oil production runs. Oil yields obtained at these conditions confirmed that the laboratory results could be duplicated at the pilot plant scale.

In addition to a discussion of the procedures used in operation of the pilot plant, this section presents detailed summaries of the material balance and yield results for all runs and lists the properties of the char, oil and gas products obtained for all runs. Evaluations of the products obtained are discussed in the following section of this report, Phase III - Product Evaluation.

PILOT PLANT PROCEDURES

Feed Preparation

About 450-900 kilograms per hour (1000-2000 pounds per hour) of feedstock is transferred pneumatically from storage bins into a stirred fluid bed drier. A propane fired jet delivers 120°C (250°F) gas to the bed at 125 cycles per second resulting in sonic energy to increase drying efficiency. The discharge from the drier is pneumatically transferred at 450-900 kg/hr (1000-2000 lb/hr) either to storage or to a vertical hammer mill for secondary shredding. Milled and dried feedstock can be returned to storage or transferred pneumatically to the pyrolysis feed bin.

Pyrolysis System

Figure II-1 presents a simplified flow diagram of the pyrolysis pilot plant. A plot plan of the equipment is shown in Figure II-2.

The GR&D four TPD pilot plant was built in 1972 as a test facility to evaluate the flash pyrolysis process (which had been successfully proven on the laboratory scale), and to obtain the heat and material balance data needed for the design of larger units. Operations after shakedown testing in 1971 were devoted primarily to processing of solid waste until early in 1974. A summary of the pilot plant operations on solid wastes through 1974 is presented below:

Feed Stock	Feed Weight lbs	Operating Time Hours
Municipal Solid Waste	32,603	1,160.2
Bark	28,193	453.8
Rice Hulls	24,228	316.0
Straw	3,761	69.6

Char Loop -

Char is dropped from a heat traced bin into a screw feeder that controls the rate at 90-900 kg/hr (200-2000 lb/hr) into a pneumatic transport line. The transport gas is developed by a 135,000 kcal/hr (530,000 Btu/hr) gas fired generator. The generator produces gas at 985°C (1800°F), which heats the char to an ignition temperature of approximately 540°C (1000°F) and transports it to the heater where

FIGURE II-1

GARRETT RESEARCH & DEVELOPMENT 4-TON/DAY PILOT PLANT FLOWSHEET

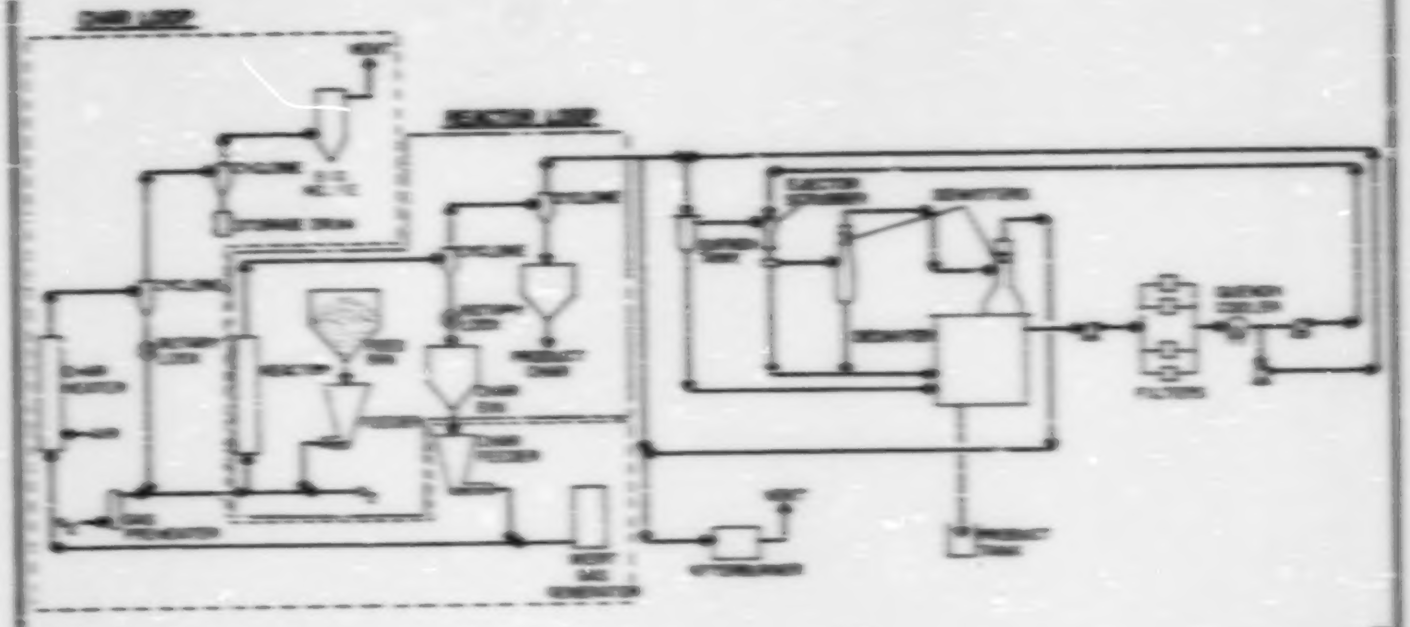
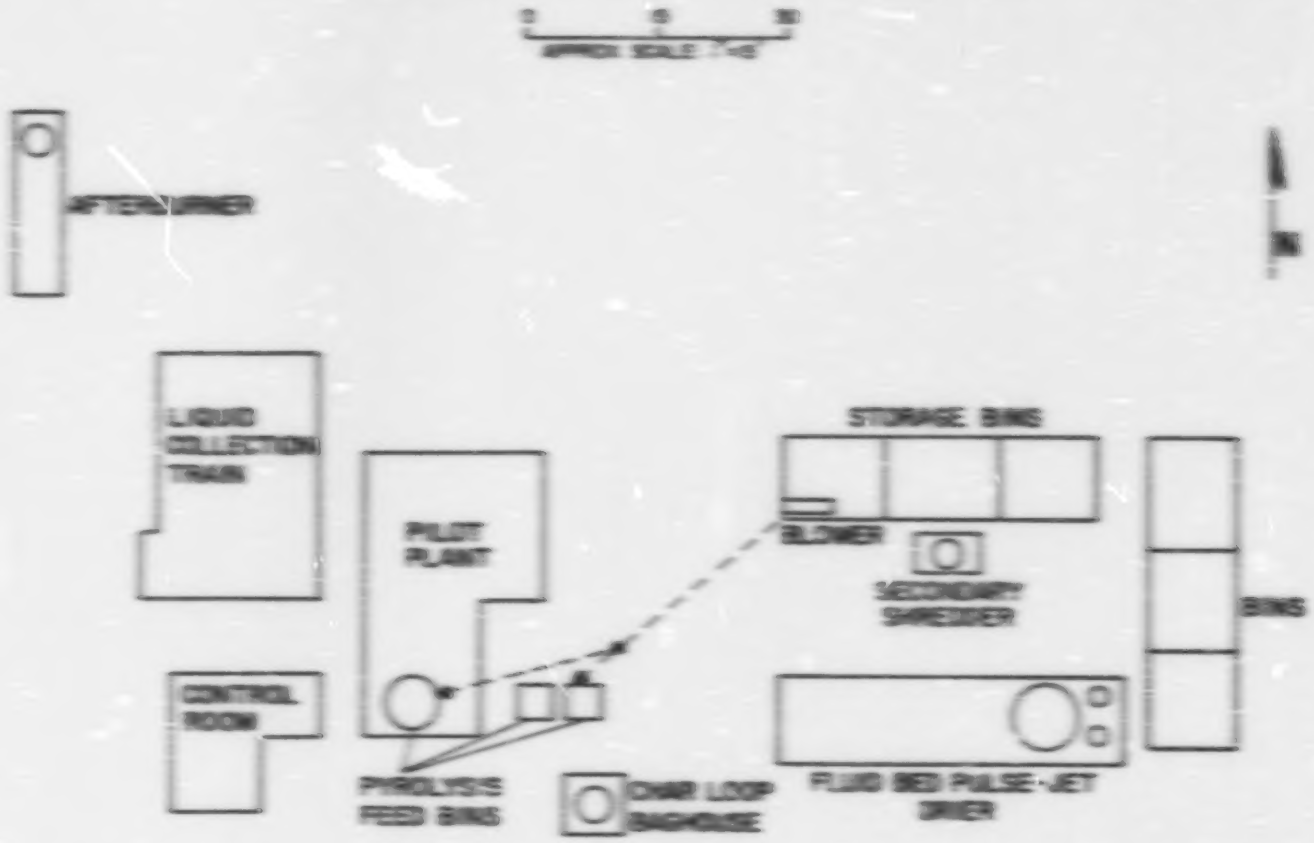

CHAR LOOP
REACTOR LOOP
VENT
CYCLONE
STORAGE DRUM
CYCLONE
CHAR HEATER
REACTOR
FEED BIN
CYCLONE
PRODUCT CHAR
CHAR BIN
CHAR FEEDER
INERT GAS GENERATOR
VENT
FILTERS

FIGURE II-1

FIGURE II-2

GR&D 4 TPD PILOT PLANT PLOT PLAN


0
5
10
APPROX SCALE 1"=10'
AFTERBURNER
N
LIQUID COLLECTION TRAIN
CONTROL ROOM
PILOT PLANT
PYROLYSIS FEED BINS
CHAR LOOP BAGHOUSE
STORAGE BINS
BLOWER
SECONDARY SHREDDER
FLUID BED PULSE-JET DRIER
BINS

partial combustion raises the temperature to 705-930°C (1300-1700°F). The hot char is separated from the transport and flue gases by a primary cyclone and the cyclone discharge is fed by rotary valve to the reactor loop or returned to the char bin depending on the desired mode of operation. Fines from attrition and combustion are removed from the gases by a secondary cyclone. If H_2S is in the flue gas, it can be removed by reaction with iron oxide in a contactor vessel. The gases then pass through a baghouse containing eight Nomex bags before venting to the atmosphere.

Reactor Loop -

The feedstock from the pyrolysis feed bin is delivered by a rotary valve into a live bin hopper where a screw feeder controls the feed rate at 13.5-135 kg/hr (30-300 lb/hr) into a pneumatic transport line. Nitrogen or recycle gas transports the feed into the pyrolysis reactor. The pyrolysis reactor is equipped with electrical wall heaters, and start-up char can be produced by direct heating. However, in normal operations, pyrolysis is conducted by circulating hot char from the char loop, and in this mode of operation, the hot particulate char is transported into the pyrolysis reactor for intimate mixing with the feed, by nitrogen or recycle gas that has been preheated by a separate tubular heater. The circulating char is removed from the pyrolysis gas stream by a primary cyclone and returned to the char bin by a rotary valve. A second cyclone removes fine product char from the gas stream and discharges it out of the system to a water jacketed char receiver. The condensibles-laden gas stream from the second cyclone is directed to the oil collection system, or to a direct gas fired afterburner if only reactor parameters are under study.

Oil Collection System -

The condensibles-laden gas stream is quenched by contacting with a recirculating immiscible oil fluid. Several types can be used and were studied at length. The one used most often was a C_{11}-C_{14} branch-chained aliphatic compound trade named AMSCO 460 by the Union Oil Co. The quenched gas passes through a venturi scrubber and a series of demister pads for removal of aerosols formed during the rapid pyrolysis reaction. The scrubbed gas can be directed through a fiberglass packed pad for final mist elimination or through a heat exchanger to condense water of reaction prior to the mist eliminator. The gas can then be exhausted to the atmosphere through the afterburner or can be recycled.

The quenching fluid is pumped by an inline centrifugal pump through basket filters and a heat exchanger from a decanter tank to a surge tank. The liquid is pumped from the surge tank by a gear pump to the venturi scrubber that drains back into the decanter tank. The liquid from the surge tank is also pumped to the quench tank by an inline centrifugal pump to control quench temperature and also drains back into the decanter tank.

Product Oil Treatment

If product oil treatment is needed, a variable rate positive displacement pump transfers product oil from the bottom of the decanter tank through basket filters to a centrifuge. The centrifuge separates the product oil from the quench fluid. The quench fluid is returned to the decanter tank and the product oil can be processed through a thin film evaporator if adjustment of the final moisture content is required.

Analyses

The feed and product streams were subjected to the analytical procedures summarized below.

Char and Feed -

These materials were subjected to ash and elemental analyses, bulk density, particle density (by fluid displacement), ash composition (by atomic absorption), feed moisture (oven dry for four hours), and particle size distribution (by sieve, and micromerograph).

Condensibles -

These were analysed for water (azeotropic distillation and Karl Fischer), quench fluid (by centrifuging and separating phases), char (filter residue from an acetone plus 5% caustic wash), ash and elemental analyses, and for COD, (if the water content was greater than 50%).

Oil Properties -

Viscosity (Saybolt Univ.), density (pycnometer), flash point (Pensky-Martens) and pourpoint were determined.

Gas -

Combined gas chromatography and mass spectrometry.

MATERIAL BALANCE

Scope and General Methods

A major objective of the pilot plant program was to measure directly the oil yields obtained during operation of the pyrolysis process at the pilot plant scale while in the char heating mode. Process conditions were held at steady state for all runs with the exception of a few short tests. The most important parameter, pyrolysis temperature, was studied in depth in the laboratory phase of this program. Based on those data, an expected optimum temperature was selected for all oil production runs, and the oil yield at these conditions was compared with the laboratory pyrolysis results. The gathering of other yield data was subordinated to the above objective to a greater or lesser degree depending upon the relative importance of the other data for corroboration of oil yield results. Accordingly, emphasis was placed on accurate measurements and analysis of the feed and liquids recovered from the oil collection system, including water byproducts.

Material balances were calculated for the pyrolysis step for each feedstock. Oil and water yields were measured directly and the gas was determined indirectly by sampling and compositional analysis. Gas yields and rates were computed from the known nitrogen carrier gas rate and the measured gas composition. Combining those results gave the char yield by difference since some of this product is consumed in the process and cannot be measured directly when operating in the char heating mode. However, the yield obtained by difference can be confirmed by comparison with the pyrolysis yields from operating in the direct heating mode which generally gives excellent mass balance closures.

Material balance data were obtained only for the pyrolysis step of the process, as calculation of an overall process material balance closure is beyond the scope of this program. Complete material balance analysis of the char heating operation was impractical for several reasons. First, the product char composition cannot be accurately determined in a mixture with startup petroleum coke. Also, the amount of char combusted cannot be accurately calculated, since inert gas generated from natural gas combustion was used for char heater solids transport, which masks the products of char combustion. Finally, operation was limited to 16 hours per day owing to manpower limitations. The daily heatup period, an unsteady state, also adds an additional complication.

An elemental balance for the pyrolysis step was made based on the mass balance calculated for the char heating runs described above. Pyrolytic char composition was obtained from the direct heating operation data. All other compositions were directly measured. This procedure permits calculation of closure for carbon, hydrogen and oxygen, based on feed, giving an independent check on the accuracy of the mass balance and, particularly, the oil yield.

Oil yield was also measured by isokinetic sampling. This technique involves taking a slipstream sample of the hot pyrolysis off-gases and condensing the oil and water in cold traps. By this procedure a measurement of oil and water yields was obtained which is completely independent of the macroscopic result.

Macroscopic Measurements

Feedstock -

Several tons of feedstock was prepared in advance, kept in storage bins, and transferred pneumatically to the feed bin in loads of about 900 kg (2000 lb). Typically, two or three loads were charged in a run. The material was sampled in the storage bin compartment just prior to transfer. Several increments were taken using a slotted tubular "thief" to assure a representative sample. Each sample was analysed for moisture (the feedstocks were hydroscopic at low moisture contents), and the weight of moisture and dry feed was calculated for each load. Then, by careful physical blending, a composite was formed for each run, and moisture, ash, and elemental analyses were made on the composite. Feed weight was recorded continuously.

Condensibles -

Typically, 70-80% of the oil yield was recovered in the primary collection vessel, the decanter. (Refer to the flow diagram, Figure II-1). The product oil is considerably denser than the quench oil (about 1.2 vs 0.8 g/cc) and settled readily to the bottom. Product oil was drawn off daily at the end of the operations and stored in drums. This batch removal procedure assured correspondence between feed weight and oil recovery for material balance calculations. Since some soluble, as well as entrained quench oil was also removed with the oil products, each drum was sampled at several levels to provide a representative averaged sample of the drum. Each sample was analysed for moisture, quench oil, and char contents. A mathematical composite was then formed for the complete run in proportion to the drum weights. These composite analyses were then used to calculate the material and elemental balances described above.

By careful control of the quench oil flow and temperature, the gas leaving the primary scrubber contained most of the byproduct water, along with some entrained product oil and quench oil. Most of the entrained oils were then removed by the total condenser and drained to a drum which was weighed, sampled, and analysed daily by the same procedure used for the product oil from the decanter. The gas leaving this condenser then passes through a mist eliminator of packed fiberglass. The net weight gain of the fiberglass element was recorded. Typically 1-3% of the oil produced was collected at this point. Oil from the fiberglass elements was analysed, and its composition was accounted for in reporting product oil composition.

Condensibles in the gas vented to the afterburner were measured by isokinetic slipstream sampling. Product oil loss was typically about 5% of the total oil. The measured quench oil and water losses agreed with their known vapor pressures. The inventory of quench oil was carefully weighed in and out to account for any solubility of product oil.

Pyrolysis of two feedstocks (tree bark and grass straw) produced from 5 to 15% wax (based upon feed) which was soluble in the paraffin quench oil in all proportions at the operating temperature. This wax yield could not be measured accurately by net change in quench inventory owing to the relatively large amount of quench oil compared to the quantity of feed processed during any typical run. Since the production of this wax fraction was not foreseen, suitable dewaxing equipment was not provided and a direct measurement could not be made. However, the wax yield was satisfactorily determined indirectly by measuring the wax concentration changes in the quench oil by vacuum distillation.

Char -

The term pyrolytic char refers to the thermal decomposition product, as distinguished from product char which has been partially burned in the char heating operation. Pyrolytic char cannot be measured directly during operation in the char heating mode. It can, however, be measured from the direct heating runs where the char is neither burned nor mixed with substitute char. Two methods were used. The preferred method was to simply remove all product char from the receiver bin, weigh, and sample it. This was done in only a few cases. Normally, the char bin weight transmitter was used. An absolute weight could not be obtained, however, due to changes in stress because of thermal expansion effects of the connecting pipes. Thus only an approximate yield result could be obtained by this measurement. For long runs (when steady state temperatures were reached) the yield of pyrolytic char was estimated by comparison of rate of weight gain of the char bin to feed rate.

Microscopic Measurements

Isokinetic Oil Yield Test -

Isokinetic sampling was developed as a means of quickly measuring oil yield. It is a useful technique for scanning the effects of operating variables and to confirm the macroscopic results. In essence, the method involves a representative sampling of the gas stream containing solids and possibly condensed products. This is done by matching the gas velocity in the sample tube to that of the process line to assure representative capture of the high momentum (larger than 1 micron) particles. Sample gas flow rate is therefore proportional to process flow via the area ratio of process pipe and sample tube areas. A collection train of four 4-liter kettles in series was used to condense and collect the vapors: one at ambient temperature, one at ice water, and two in a dry ice-trichloroethylene bath. The gradual temperature reduction is necessary to minimize plugging problems. The kettles were followed by a submicron filter to remove final traces of oil aerosol and then a positive displacement meter calibrated against a wet test meter. While process pressure was adequate for flow, a needle valve followed by a vacuum pump was found to be more effective configuration, since a high pressure drop results in better flow control. Very accurate measurements of feed weight and composition are required for this test. Feed material was weighed to within 0.05 kg (0.1 lb) and loaded into the feeder hopper. Generally the feed weight exceeded 45 kg (100 lbs). A limit to accuracy in this method is the process gas flow which was measured to within 2%, relative, which is equivalent to 1% absolute accuracy of the reported yield.

Gas Yield -

The gas yield was calculated from gas composition, total gas flow, and feed rate measurements. Integrated gas samples of 15-30 minutes duration were collected. This was done simultaneously with the isokinetic oil yield tests for which the feed rate and composition during the sampling period were known accurately. The integrated sampling method averages gas composition variations due to normally occurring small fluctuations of feed rate and gas flow.

EXPERIMENTAL RESULTS AND DISCUSSION

The 4-ton-per-day pilot plant was used to obtain process engineering data to design commercial scale demonstration plants for the flash pyrolysis of industrial solid wastes. The feedstocks processed were Douglas Fir tree bark, rice hulls and rye grass straw. The primary objectives were to determine yields both by macroscopic balance and by isokinetic stream sampling, and the production of sufficient quantities of pyrolysis products (char, oil and gas) for characterization and evaluation.

The program outline was (1) preparation of feed stock for flash pyrolysis (particle size, etc.); (2) production of start-up char by electrical heating; (3) determination of product char properties; (4) confirmation of operating conditions for optimum yields; and (5) production of oil for study and evaluation.

Feed Handling Procedures

Table II-1 presents a summary of the feed analyses used for pilot plant runs. Douglas fir tree bark required drying and milling before it was fed to the plant. Tree bark char was produced for start-up and the oil collection system was operated periodically during char production to evaluate the collection system and train personnel. Circulation of hot tree bark char for reactor heating was not found to be feasible in the existing system which originally had been designed for coal conversion. Consequently, petroleum coke was used as the circulating solid heat carrier in subsequent pilot plant runs to determine operating conditions and oil yields.

Rice hulls were processed as received without any feed preparation. The char produced appeared to behave satisfactorily in the pilot plant during char circulation studies, but its recovery proved to be somewhat insufficient with the existing cyclone design. Thus, operations for the production of rice hull oil also utilized petroleum coke as the circulating heat transfer media.

The only feed preparation for rye grass straw was milling. A quantity of oil was produced utilizing petroleum coke. The resulting composite char confirmed expectations that the existing equipment designed for coal could not have circulated the straw char effectively.

Table [illegible]. [illegible] ANALYSIS SUMMARY

Run Number	Feed-stock	Mesh Analysis Cumulative % Retained							Ultimate Analysis								
		20	40	100	150	200	325	-325	H_2O	V.M.	Ash	C	H	N	S	Cl	O
37-73	Bark	8.0	43.6	63.4	73.4	81.6	90.6	9.4									
		5.8	35.0	56.5	66.7	76.0	87.7	12.3									
		6.5	30.2	46.4	57.8	67.1	80.8	19.2									
		4.6	20.4	33.4	43.8	53.3	70.8	29.2									
39-73	Bark	4.2	27.8	45.5	57.9	62.1	72.1	27.9									
		15.7	42.2	55.9	68.2	76.6	83.5	16.5	5.5	-	22.1	-	-	-	-	-	-
49-73	Bark	9.8	29.2	49.8	64.6	73.5	83.5	26.5	5.1	70.55	4.36	55.90	6.13	1.36	0.09	-	37.6
50-73	Bark	26.5	51.4	65.9	73.5	78.0	86.2	13.3	5.4	-	-	-	-	-	-	-	-
		20.6	45.2	59.5	68.1	74.1	82.8	27.2	6.4	69.52	9.75	54.07	6.22	0.37	0.09	-	29.25
		18.1	41.6	56.2	66.4	73.2	83.3	17.7	4.2	-	-	-	-	-	-	-	-
52-73	Bark	26.7	52.2	67.8	74.9	80.8	86.9	13.1	4.9	-	-	-	-	-	-	-	-
57-73	[illegible]	41.7	81.4	92.2	95.0	96.5	97.5	2.5	6.32	59.22	17.05	41.57	5.56	0.35	0.16	0.05	-
									-	63.32	18.20	44.33	5.29	0.37	0.27	0.16	31.49
63-73									-	-	18.91	40.80	5.40	0.41	0.05	0.13	35.10
64-73									-	-	19.39	39.75	5.30	0.35	0.22	0.09	35.03
66-74	Straw	5.3	35.5	61.4	75.9	84.2	90.8	10.2	5.9	-	8.56	42.04	6.57	0.50	0.22	0.35	-
									-	-	9.11	45.53	6.20	0.53	0.25	0.37	-
									5.9	-	8.50	42.26	6.25	0.53	0.35	0.35	-
									-	-	9.62	44.91	5.92	0.56	0.38	0.37	38.41
									6.6	-	6.81	42.46	6.21	0.53	0.36	0.32	-
									-	-	6.44	45.48	5.86	0.57	0.39	0.36	40.92

Summary of Operations

Initial operation to produce tree bark char was conducted over a period of 6 weeks, pyrolyzing 5069 kg (11,175 lbs) of tree bark by direct heating during 6 runs totalling 136 hrs of feeding time, and producing about 1360 kg (3000 lbs) of tree bark char. Over 900 kg (2000 lbs) of tree bark pyrolysis oil was collected during these runs as a secondary objective to evaluate the oil collection system and train the operating personnel. The presence of a wax fraction in the tree bark pyrolysis oil was noted and the operating problems created by the wax phase in the operation of the oil collection system were resolved during these char production runs.

Tree bark char combustion and cyclone efficiencies were studied over a two week period consisting of four runs totaling 23 hours of char circulation. The equipment designed for coal proved to be unsatisfactory for the lighter density tree bark char. Rather than spend considerable time and money redesigning and modifying existing equipment, higher density petroleum coke was used as the circulating solid. However, the reactor feed rate then had to be decreased, owing to the lower reactivity of this char and consequent lower temperature upon combustion in the char heater.

The operating conditions for the production of pyrolytic oil from tree bark were established during four runs over a four week period feeding 5450 kg (12,000 lbs) of tree bark for 140 hrs. Wax associated problems were resolved during these runs and a technique of controlling the moisture content of the product oil was established. The subsequent tree bark pyrolysis oil production run covered a two week period feeding 2270 kg (5000 lbs) of tree bark for 105 hrs and collecting 681 kg (1500 lbs) of pyrolytic oil.

Rice hull char production was conducted over a period of two weeks, pyrolyzing 3360 kg (7400 lbs) of rice hulls using direct heating during one run of 105 hrs and producing approximately 1090 kg (2400 lbs) of rice hull char. Rice hull char combustion and cyclone efficiencies were studied over a two day period consisting of one run of 14 hrs. The equipment designed for coal appeared to operate satisfactorily with rice hull char.

Circulation of rice hull char was thus attempted during initial operation for the production of rice hull oil. However, during a one week period, 1415 kg (3115 lbs) of rice hulls was fed over a total 24 hours operating time, and the high char content of the pyrolytic oil indicated that the cyclone efficiency was again unacceptably poor. Therefore, petroleum coke was again used as the circulating heat transfer solid. The production of pyrolytic rice hull oil was then conducted over a period of three weeks, feeding 7270 kg (16,000 lbs) of rice hulls during three runs totaling 144 hrs of feeding time, and collecting 1270 kg (2800 lbs) of oil.

Pyrolytic oil from rye grass straw was produced during one run over a two week period, feeding 1820 kg (4000 lbs) of straw for 48 hrs with 70 hrs of char circulation and collecting 500 kg (1100 lbs) of oil.

Bark Char Production Runs -

Run 37-73 - The first tree bark char production run (37-73) was 1680 kg (3700 lbs) of tree bark processed over 51.8 hrs for an average rate of 32.3 kg/hr (71 lbs/hr). The feed rate was limited by the electrical heat flux capacity of the reactor wall heaters which was less than 3.3 kw/m (1 kw per foot). The time-average pyrolysis temperature in the electrically heated reactor was 513°C (957°F). The char produced was 479 kg (1055 lbs) for a yield of 29 wt %. The oil product containing 20% water was successfully pumped and filtered at 60-66°C (140-150°F). The wax fraction remained in solution in the quench liquid above 49°C (120°F).

Run 38-73 - During the second tree bark char production run (38-73), 986 kg (2170 lbs) was processed over 33.9 hrs for an average rate of 29 kg/hr (64 lbs/hr). The reactor was heated electrically to a time-average pyrolysis temperature of 502°C (936°F). A total of 332 kg (731 lbs) of char was produced for a yield of 34%.

The oil collection system was then insulated and quench fluid rates were reduced during this run to achieve a higher quench system temperature and avoid the problem of wax deposits. The higher collection system temperature resulted in a low water content oil (about 8% water) that was very viscous, resembling pitch. No effort was made to further treat this oil.

Runs 39-73, 40-73, 41-73 - The third, fourth and fifth bark char production runs (39-73, 40-73, and 41-73) used 281 kg (620 lbs), 422 kg (930 lbs) and 590 kg (1300 lbs) of tree bark, processed over 8.6 hrs, 11.2 hrs and 17.2 hrs for average rates of 32.9 kg/hr (72.5 lbs/hr), 37.6 kg/hr (82.9 lbs/hr) and 34.2 kg/hr (75.3 lbs/hr) respectively. The reactor was electrically heated to time-average pyrolysis temperatures of 493°C (921°F), 494°C (922°F) and 499°C (930°F). Total char collected for the three runs was 267 kg (587 lbs) for a yield of 21%.

The oil collection system was carefully studied to optimize the oil moisture control methods. The bark oil collected during these runs varied in moisture content from 13% to 20%. Blends of the oil were made for viscosity and density measurements as functions of water content and temperature. Filtration of oils heated to 160-180°F revealed that successful filtration depends not only on temperature but also on water content; this is probably an effect of dispersion of the particles as well as an effect of viscosity. Operation of a simple dewaxing unit was also tested on a small quench fluid stream during these runs, but temperatures below 120°F were not achieved and the wax remained in solution.

The temperature control of the entire liquid collection system was again reviewed. The addition of a [illegible] heater to raise the temperature of the circulating quench fluid greatly improved control from this point forward.

Runs 42-73, 43-73, 44-73 - The last three bark char production runs (42-73, 43-73 and 44-73) used 210 kg (460 lbs) of tree bark over 5.9 hrs for an average rate of 35.4 kg/hr (77.9 lbs/hr), 254 kg (560 lbs) over 6.9 hrs for an average rate of 36.8 kg/hr (81.1 lbs/hr), and 643 kg (1415 lbs) over 20.2 hrs for an average rate of 31.8 kg/hr (70.0 lbs/hr) respectively. The time-average pyrolysis temperatures were 505°C (941°F), 491°C (916°F), and 495°C (924°F) respectively.

The product char from these runs was left in the char bin for subsequent combustion tests in the char heater. However, char weights and therefore char yields were not determined for these runs.

Test operations of the oil collection system indicated that pyrolytic oil could be recovered without using the centrifuge to remove quench liquid and without employing the thin film evaporator for further water removal. Only a cursory investigation of wax removal from the quench fluid was made during these runs. The affect of increasing concentrations of soluble oil and wax in the quench fluid was left for study during the later oil production runs.

Rice Hull Char Production Run 57-73 -

Rice hull char was produced during one run by feeding 3340 kg (7360 lbs) of rice hulls over 104.6 hours for an average rate of 32.0 kg/hr (70.4 lbs/hr) and producing approximately 1090 kg (2400 lbs) of char. The reactor was heated electrically for an average pyrolysis temperature of 504°C (940°F). The char produced remained in the bin for subsequent combustion tests; the change in the bin weight recorder indicated a yield of approximately 40%. While the oil collection system was not operated, integrated isokinetic gas samples indicated gas yields of 11.0 and 9.3 wt % were achieved on a dry feed basis.

Bark Oil Production Runs -

Run 49-73 - The first Douglas fir tree bark production run (49-73) used 1660 kg (3660 lbs) of tree bark for 34.7 hrs for an average rate of 57.5 kg/hr (126.4 lbs/hr). The reactor was heated by circulating petroleum coke at 527°C (980°F), heated to an average temperature of 698°C (1288°F) by partial char combustion. The low reactivity of the petroleum coke limited the char circulation rate to 182 kg/hr (400 lbs/hr) since the combustion of petroleum coke was not rapid enough to maintain the desired temperature at higher circulation rates. The combustion of petroleum coke and product char was also limited by the excess air that could be obtained from the inert gas generator system. Increases in excess air resulted in decreases in the carrier gas temperature and the increase in char combustion did not compensate for the loss in sensible heat. The average pyrolysis temperature for this run was 515°C (959°F).

The collection system was operated during 31 hrs at [illegible]°C (112°F), and the collected oil was left in the system to combine with the oil collected during the next run. Thus no separate oil yield was determined for this run. Successful removal of wax was achieved using -10°C (20°F) glycol as a coolant through a coil in a 208 liter (55 gallon) drum. The operation was a simple batch procedure performed as time permitted and providing data sufficient for design of a continuous operation.

Run 50-73 - The second tree bark oil production run (50-73) used 1060 kg (2330 lbs) of tree bark for 13.9 hrs for an average rate of 76 kg/hr (167 lbs/hr). The reactor was 491°C (916°F), heated by circulating petroleum coke at an average temperature of 681°C (1258°F).

The collection system was operated at 48°C (118°F) and the overall yield for the 1st and 2nd production runs was 22% collected in the main receiver on a dry oil/dry feed basis. (This yield does not include wax, quench oil solubles, collections at demister pads, or vent losses). The integrated isokinetic sample gave an estimate of the liquid yields that would have been obtained if all sources had been collected. On a dry feed basis the total oil yields from these runs were:

Bark oil (dry)	39.0%	(including wax)
Pyrolytic water	17.8%	

The wax concentrate from the batch dewaxing operation was analyzed and found to be only 13% wax and 87% quench liquid. Apparently the wax traps a significant amount of quench liquid as it is cooling and the resulting solid actually has a relatively low wax concentration.

Run 51-73 - The third tree bark oil production run (51-73) used 1785 kg (3930 lbs) of tree bark over a 30.8 hr period for an average rate of 58 kg/hr (127.7 lbs/hr). The reactor was maintained at 490°C (915°F) by circulating petroleum coke at 204 kg/hr (450 lbs/hr) at a temperature of 747°C (1375°F). The collection system was operated at 48°C (118°F), and 342 kg (753 lbs) of oil was drained from the primary receiver for a 20.4% primary collection on a dry oil/dry feed basis. The remaining oil yield was not collected.

Run 52-73 - The fourth bark oil production run (52-73) used 847 kg (1865 lbs) of tree bark over 13.5 hrs for an average rate of 62.7 kg/hr (138 lbs/hr). The reactor was maintained at 476°C (888°F) by circulating 182 kg/hr (400 lbs/hr) of petroleum coke at 808°C (1487°F). The collection train was operated at from the primary receiver for a recovery of 24.6 wt % dry bark oil/dry feed basis. The remaining oil yield was not collected.

Run 53-73 - The final Douglas fir tree bark pyrolytic oil production run (53-73) was made with emphasis on a complete macroscopic material balance. A total of 2326 kg (5129 lbs) of tree bark was processed over a 47 hr period for an average rate of 49.5 kg/hr (109 lbs/hr). The reactor was heated to an average pyrolysis temperature of 474°C (886°F) by circulating 204 kg/hr (450 lbs/hr) of petroleum coke heated to 828°C (1522°F). The collection system was operated at 52°C (126°F) with improvements in the primary receiver that raised the primary collection to 30% (compared to 21% during earlier runs).

The final macro-balance gave 39.7 wt % oil yield vs 40 wt % by the integrated isokinetic samples of the product stream. Integrated isokinetic samples were also taken from the vent line to determine oil losses and gas yields. The break-down of the overall yields on a dry feed basis was:

Pyrolytic Oil	36.9	39.7
Wax	2.8	
Water	15.5	
Gas	16.0	
Char (by diff.)	28.8	
	100.0	

An attempt to filter the bark oil was not successful. A worm-type positive displacement pump operated satisfactorily but adequate filtration and filtration rates could not be achieved. The small particle size of the char (50% less than 12 micron) probably results in blinding of the filter bags by filling the interstices, preventing buildup of a filter cake. Larger filter area would result in excessive oil loss. (The pilot plant centrifuge is designed for liquids and would not operate for any reasonable length of time while attempting to remove solids).

Rice Hull Oil Production Runs -

The objectives of the rice hull pyrolytic oil production runs were:

1. Produce rice hull pyrolytic oil for combustion tests.
2. Test solubility limits of rice hull oil in the quench fluid.
3. Obtain macroscopic yield data.
4. Obtain gas yield data.
5. Obtain isokinetic yield data.
6. Obtain vent gas aerosol loss data.
7. Establish techniques to control water content of the product oil.

Run 59-73 - The first rice hull oil production run (59-73) used 1413 kg (3115 lbs) of rice hulls over 26.8 hrs for an average rate of 52.7 kg/hr (116 lbs/hr). The reactor was heated to 489°C (912°F) by circulating rice hull char heated to an average of 708°C (1307°F) by partial combustion in the char heater.

The collection system was operated but due to the short duration of the run, oil production was too limited for an adequate material balance or conditioning of the quench liquid.

Excessive char carry-over was observed and attributed to attrition and combustion of the rice hull char resulting in particle sizes too small for efficient collection by the pilot plant cyclones. The high ash content of rice hull char is not only undesirable in the pyrolytic oil product, but the heat capacity of the circulating char steadily decreased as the ash content of the char built up during the run.

Inspection of char loop piping revealed high ash content and related high bulk density deposits in horizontal piping sections of the pilot plant. Therefore, subsequent rice hull pyrolytic oil runs were made using the less reactive, but lower ash content petroleum coke as the circulating solid.

Run 63-73 - The second rice hull oil production run (63-73) used 1716 kg (3784 lbs) of rice hulls over 33.7 hrs for an average rate of 50.9 kg/hr (112.3 lbs/hr). The reactor was maintained at 481°C (897°F) by circulating petroleum coke at 204 kg/hr (450 lbs/hr) heated to 618°C (1144°F) by partial combustion. The collection system was operated at 58°C (136°F) utilizing the 4.88m (16 ft) heat exchanger for improved oil moisture control. The vent loss of oil was measured to be 1.8 wt % on a dry feed basis.

Comparative yields on a dry feed basis were:

	Macro	Isokinetic
Rice Hull Oil	26.0	21.2
Pyrolytic Water	20.4	22.3

Run 64-73 - The third rice hull oil production run (64-73) was a continuation of Run 63-73 to monitor the change in macroscopic yields during dissolution into the quench liquid of the soluble fraction of rice hull oil ("conditioning"). A total of 1943 kg (4284 lbs) of rice hulls was fed over 35 hrs for an average rate of 55 kg/hr (120.0 lbs/hr). The reactor was maintained at 484°C (903°F) by circulating petroleum coke at 295 kg/hr (650 lbs/hr) at 675°C (1246°F). The collection system was operated at 57°C (134°F) and comparative yields were:

	Macro	455°C(850°F) Isokinetic	516°C(960°F) Isokinetic
Rice Hull Oil	25.3	25.5	25.0
Pyrolysis Water	21.0	20.4	21.3
Gas	-	5.4	5.8
Char (by difference)	-	48.7	48.9

Run 65-73 - The final rice hull oil production run (65-73) was for continued "conditioning" of the quench fluid by soluble rice hull oil components using 2479 kg (5465 lbs) of rice hulls over 50.8 hrs for an average rate of 48.8 kg/hr (107.6 lbs/hr). The reactor was maintained at 488°C (910°F) by circulating petroleum coke at 295 kg/hr (650 lbs/hr) at 683°C (1262°F). The collection system was operated at 57°C (137°F) and comparative yields were:

	Macro	516°C (960°F) Isokinetic	488°C (910°F) Isokinetic	460°C (860°F) Isokinetic
Pyrolytic Oil	22.1	23.7, 20.0	22.2, 21.3	22.0, 22.7
Pyrolysis Water	22.4	20.9, 18.8	21.0, 18.4	18.4, 19.7

An expected increase in oil recovery, as the quench liquid became "conditioned", did not occur; in fact, macroscopic yields decreased. These lower oil yields were thought to result from a larger feed particle size and a higher moisture content, as indicated by a comparison with bench scale results. However, subsequent isokinetic tests with milled and dried rice hulls did not show substantially higher oil yields.

Grass Straw Oil Production, Run 66-74 -

The objectives of the rye grass straw pyrolytic oil production run were; (1) determine the macroscopic yield, (2) determine properties of grass straw pyrolytic oil, (3) determine an integrated isokinetic yield, (4) determine the gas yield.

The straw pyrolytic oil production run (66-74) used 1708 kg (3765 lbs) of straw over 48.0 hrs for an average rate of 35.6 kg/hr (78.4 lbs/hr). The reactor was maintained at 483°C (902°F) by circulating petroleum coke at 318 kg/hr

(700 lbs/hr) at 658°C (1216°F). The collection system was operated at 57° (135°F). Liquid losses in the vent were determined to be 1.1 wt % oil and 3.7 wt % water, while the gas yield was calculated at 5.5 wt % on a dry feed basis. Comparative yields were:

	Macro	Isokinetic
Pyrolytic Oil (Including wax)	32.2	28.0, 26.8
Pyrolytic Water	24.9	26.6, 24.7

An inspection of the piping at the completion of this run revealed a composite char with an angle of repose of 80-90° vs the 25-30° exhibited by the initial char. The inability of this char to flow would account for high char carry-over and the erratic feed rates experienced during this run.

Other Pilot Plant Operations

Douglas fir tree bark char was conditioned for subsequent studies on activation by devolatilization and partial combustion, and cyclone efficiencies were studied, during runs 45-73, 46-73, 47-73, and 48-73. The overall cyclone efficiency was only 83%, and this is attributed to the low bulk density of the char and the high length-to-diameter ratio of the char particle shape. The char captured by the second stage cyclone was 50% minus 325 mesh. Experiments revealed that tree bark char offers little resistance to flow and appreciable amounts of gas leaked upward through the char hopper into the cyclones which could have contributed to low cyclone efficiency. Gas leakage upward through the char could also result in fluidization which makes the actual char circulation rate indeterminate and therefore possibly higher than the capacity of the rotary valves.

Rice hull char was conditioned for activated charcoal studies by devolatilization and partial combustion, and cyclone efficiencies were studied during run 50-73. The rice hull char was devolatilized at 704°C (1300°F) at an estimated circulation rate of 91 kg/hr (200 lbs/hr) for 10.5 hrs, reducing the char inventory from about 556 kg (1226 lbs) to approximately 454 kg (1000 lbs). The combustion of rice hull char was performed for three hours at an estimated circulation rate of 136-159 kg/hr (300-350 lbs/hr), further reducing the char inventory from about 454 kg (1000 lbs) to approximately 250 kg (550 lbs).

Cyclone efficiencies appeared to be 99-100% during char devolatilization and 96-99% during rice hull char combustion, but a sudden system upset prevented accurate measurements.

MATERIAL BALANCE RESULTS AND DISCUSSION

Oil and Water Yields

The pilot plant results confirm that a moisture free oil yield of 42.8% can be obtained from the pyrolysis of Douglas Fir bark on a moisture-and-ash-free (MAF) feed basis. This yield includes the bark wax and compares favorably with the laboratory reactor result. Pyrolytic oil yields from rice hulls and straw are somewhat lower at 30.2% and 33.3% respectively. The cause of this deviation from the earlier laboratory reactor phase was not explored experimentally. However, in all cases, the feedstock for pilot plant operation was of considerably coarser size than that used for the laboratory phase. Tree bark particle size for the pilot plant was in the order of 70% above 200 mesh, and rice hulls and straw 95%. Feedstock for the laboratory reactor was generally ground through 200 mesh except for a few tests to check the effect of coarse feed on oil yield. In those tests coarser particles were shown to be detrimental to oil yield. In setting the conditions for pilot plant runs it was anticipated that the longer residence time in this unit of approximately one second, compared to 0.3 in the laboratory would compensate for the larger particle size. Although no firm experimental verification of this could be obtained, the pilot plant results on tree bark are consistent with this theory. The results do suggest however, that rapid heat transfer to very small feed particles is the key factor in flash pyrolysis employing very short residence times. Although the oil yields from rice hulls and straw fell somewhat short of the laboratory reactor results, the yields from tree bark and straw are approximately twice the Fischer Assay value and the yields from rice hulls are 50% greater. In this regard the results confirm the advantage of rapid heating and rapid quenching of the product vapor.

The yields of oil and water were obtained during the oil production runs (operating in the char heating mode). The methods used were described in a preceeding section. A summary of the macroscopic data is given in Table II-2. The data shown correspond to all feed and product collections for the entire run. They are not instantaneous (or rate) values. With the exception of the vent loss (which was always small), the product weights and analyses are all direct measurements.

Table II-2. MACROSCOPIC LIQUID YIELD DATA, OIL PRODUCTION RUNS

Operating Conditions:

Char heating mode
Reactor temperature 482°C (900°F)
Reactor carrier gas - nitrogen

Run Number	53-73	63-73	64-73	65-73	66-74
FEEDSTOCK					
Type	Tree Bark	Rice Hulls	Rice Hulls	Rice Hulls	Grass Straw
Moisture, wt %	3.7	8.9	7.5	7.0	5.6
Ash, wt % (db) [a]	7.3	18.9	19.4	20.1	9.1
Weight, lb (db)	4890	3446	3963	5080	3550
YIELD, wt % (db)					
Oil					
Primary Decanter	30.5	19.2	19.4	15.7	20.6
Condensers	4.0	5.4	5.6	5.0	8.8
Vent Loss	1.3	1.4	1.4	1.4	1.1
TOTAL	35.8	26.0	26.3	22.1	30.3
Wax	2.8	nil	nil	nil	1.9
Water					
Oil Moisture	5.1	3.9	4.0	3.3	3.8
Condensers	12.3	22.1	22.8	23.4	23.5
Vent Loss	3.1	4.3	2.3	3.3	3.7
Feed Moisture [c]	(4.2)	(9.8)	(8.1)	(7.6)	(5.9)
TOTAL	16.3	20.5	21.0	22.4	24.9
YIELD, wt % (MAF [b])					
Oil	39.8	32.1	31.4	28.0	33.3
Wax	3.0	nil	nil	nil	2.1
Water	18.7	25.3	26.0	28.0	27.4
FISCHER ASSAY					
Tar, wt % (MAF [b])	18		20		19

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[a] db = dry basis feed and products
[b] MAF = moisture-and-ash-free basis
[c] Moisture in feed, kgs/100 kg dry feed

The oil production operations consisted of eight runs: four on tree bark, three on rice hulls, and one on grass straw. Complete yield data were obtained for five runs: one tree bark run and all the rice hull and grass straw runs. Only partial yield data were obtained during the first three tree bark runs since during this period the product quench system was refined, improving its oil collection efficiency in the primary decanter tank from about 50% in the first run (49-73) to 80% in the last tree bark run (53-73). Measurement, sampling and analysis techniques were also refined during the first tree bark runs. Procedures for control of the product oil moisture were also refined. Details of the macroscopic recovery data are given at the end of this section (Tables II-15 through II-19). The operating data are summarized in Table II-3. Conditions were generally the same for all runs, except for variations in feedstock preparation described previously. Several isokinetic oil yield tests were made to corroborate the macroscopic oil yield results. Although considerable care was exercised in recovering or accounting for all oil produced, the isokinetic tests were made to assure that no oversights or consistent bias occurred. A description of the tests was given in the procedure section. It is reemphasized here that the isokinetic measurements are wholly independent of the macroscopic result. Further, the results are directly comparable, because the procedures used to analyse for water, char and oil were identical for all determinations. The isokinetic oil yield results are summarized in Table II-4 and compared to the macroscopic results.

Eleven isokinetic tests were made during the rice hull runs. The results of these tests are given in Table II-5. The original purpose for all these tests was to determine oil yield as a function of temprature. When the initial results indicated the oil yield to be lower than expected, replications were made. These and the macro yields were all in good agreement.

Because the rice hull oil yields were below the expected results, a review of the laboratory reactor data was made which revealed that yields were generally lower when processing coarser, wet feedstocks. The rice hull feed for the pilot plant was processed as received, 95% +200 mesh and 8-9% moisture. Two additional tests were therefore made processing material which had been oven-dried (1-2% moisture) and screened through 20 mesh to reduce the +200 mesh to 85%. The latter was an expedient in lieu of custom grinding due to program time constraints. However, some improvement could be expected if the hypothesis were true, and indeed the oil yield was found to increase by 4%.

Table 3-1. [illegible]

Run Number	Feed-Stock	Feed Time hrs	Feed Rate kg/hr	Char Rate kg/hr	Temperature, °C Gas Outlet	Char Heater Outlet	Char to Reactor	Reactor Inlet	Reactor Outlet	Collection Train
49-73	Bark	25.75	56.1	181	537	690	603	478	515	44
50-73	Bark	13.85	73.7	110	491	681	622	530	491	48
51-73	Bark	16.77	57.9	206	–	747	627	488	476	48
52-73	Bark	13.49	62.7	181	–	809	671	479	478	52
53-73	Bark	46.59	45.6	204	480	[illegible]	609	488	479	52
59-73	Rice Hulls	21.57	61.2	348	467	709	610	[illegible]	487	45
63-73	Rice Hulls	11.09	58.9	206	465	610	558	471	481	38
64-73	Rice Hulls	35.02	55.5	295	456	676	582	479	484	57
65-73	Rice Hulls	50.88	48.0	285	467	687	552	473	488	58
66-74	Grass Straw	47.99	35.6	210	356	690	566	451	482	57

Table II-4. MACROSCOPIC AND ISOKINETIC LIQUID YIELD DATA

(MOISTURE-AND-ASH FREE BASIS)

	Tree Bark	Rice Hulls	Grass Straw
Macroscopic Data			
Yield, wt %			
Oil and Wax	42.0	30.2	27.4
Water	16.7	26.6	27.6
Isokinetic Data[a]			
Number of Tests	2	11	2
Yield, wt %			
Oil and Wax	42.8	26.7	30.0
Water	30.0	25.3	28.1
Fischer Assay			
Tar Yield, wt %	18	20	19

---

[a] Slipstream sampling of product vapors and collection in cold traps (See text).

Table II-5. SUMMARY OF [illegible] OIL YIELD TESTS - RICE HULLS

Rice Hulls as-received (95% +200 mesh, 8-9% moisture)

Test #	Reactor Temperature °C	°F	Yield, wt % (basis: dry feed) Oil	Water
63-73-H	454	850	21.1	22.4
64-73-A	451	850	25.5	20.4
64-73-B	516	960	24.0	21.3
65-73-B	516	960	23.7	20.9
65-73-C	488	910	22.2	21.0
65-73-D	460	860	22.0	19.4
65-73-E	460	860	22.7	19.6
65-73-F	488	910	21.3	18.6
65-73-G	516	960	20.0	18.8
Average			22.2	20.2

Dried & Screened Rice Hulls (85% +200 mesh, 1-2% moisture)

67-74-A	482	900	25.8	21.2
67-74-B	482	90F	26.3	20.5

The effect of temperature on oil yield was negligible over the range tested, 455-516°C (850-960°F). However, this may not always be generally true. In recognition of the effect of coarse feedstock, particle heatup rate may have been the controlling factor in these tests and the variation of the final temperature within a narrow range, may have been of lesser importance. For smaller particles with faster heat-up rates and hypothetically higher oil yield, the yield could show more sensitivity to reactor temperatures.

Gas Yield

Gas yield and composition determinations were made as described in the procedural section. Again, these were conducted simultaneously with the isokinetic tests, because calculated yields depend upon the ratio of gas and feed rates, and the latter was determined accurately during all isokinetic tests. These results are summarized in Tables II-6, II-7, and II-8. The data are fairly reproducible and show some sensitivity with regard to the process variables of feedstock and temperature.

Char Yield

Accurate determination of char yield was outside the scope of this program since little information could be obtained when operating in the char heating mode. However, some information was obtained from char production runs when operating in the direct heating mode. The general approach, and some of the limitations, were discussed in the procedural section. An additional consideration is that the final temperature for the electrical heated runs was 50°F higher than for the char heated runs. The magnitude of this effect may be small in light of the relative insensitivity of the oil, water and gas yields with respect to final temperature. With these limitations in mind, the char composition data can nevertheless be used to close the elemental balance. In addition, the char yield from direct heated runs can be compared to the yields from the char heated runs by accounting for the weight difference. These results are presented below.

One direct measurement of char yield, and several char compositions, were obtained during the tree bark char production runs 37-73 and 38-73 when the receiver bin was cooled and the entire contents transferred to storage, which allowed accurate weighing and sampling.

Rice hull char production was conducted in one long run during which the receiver bin was filled and only partially emptied. Yield estimates in this case were made indirectly via the rate of weight gain indicated by the bin scale. Composition data were obtained on two drums of char removed from the receiver bin.

Table II-6. TREE BARK GAS YIELD AND COMPOSITION

Run	53-73	53-73
Date	6/15	6/15
Time	1045	1247
Reactor Temperature, °C	477 (890°F)	477 (890°F)
Feed Rate, kg/hr	51.7	52.6
Feed Rate, lb/hr	(114)	(116)
Feed Moisture, wt %	4.7	4.7
Gas Yield		
Wt %, dry feed	15.8	17.8
Nm^3/kg dry feed	0.114	0.123
(SCF/lb dry feed)	(1.83)	(1.96)
Gas Composition, mol %		
H_2	9.96	5.56
CO	35.96	36.28
CO_2	45.05	50.03
CH_4	1.15	1.09
C_2H_4	5.43	4.77
C_2H_6	0.62	0.51
C_3H_6	0.91	0.86
C_3H_8	0.00	0.04
C_4^+	1.24	1.08
Molecular Weight	32.5	34.4
Gross Heating Value, kcal/Nm^3	1781	1915
(Btu/SCF)	(200)	(215)
Elemental Analysis		
Wt %, C	36.35	35.54
H	1.71	1.24
O (by difference)	61.94	63.22

[illegible]

Run	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Test	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]			[illegible]	[illegible]
Date	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
Time	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
Reactor Temperature, °C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
(°F)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Feed Rate, kg/hr	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
(lb/hr)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Feed Moisture, wt %		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Gas Yield										
wt %, dry feed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
m^3/kg dry feed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
SCF/lb dry feed	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Gas Composition, mol %										
H_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CO_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CH_4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_2H_4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_2H_6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_3H_6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_3H_8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_4^+	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Molecular Weight	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Gross Heating Value, kcal/m^3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Btu/SCF	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Elemental Analysis										
wt % C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Char by difference	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

a [illegible]
b [illegible]

Table II-8. GRASS STRAW GAS YIELDS AND COMPOSITION

Run	66-74	66-74
Date	2/09	2/11
Time	1155	1126
Reactor Temperature, °C	482 (900°F)	482 (900°F)
Feed Rate, kg/hr	39	39
Feed Rate, lb/hr	(86)	(86)
Feed Moisture, wt %	6.7	6.7
Gas Yield		
Wt %, dry feed	5.54	5.48
Nm^3/kg dry feed	0.047	0.045
(SCF/lb dry feed)	(0.75)	(0.72)
Gas Composition, mol %		
H_2	2.17	3.00
CO	80.68	79.01
CO_2	7.86	12.66
CH_4	4.07	3.65
C_2H_4	3.43	0.41
C_2H_6	0.71	0.36
C_3H_6	0.10	0.05
C_3H_8	0.00	0.00
C_4+	0.00	0.00
Molecular Weight	28.17	28.86
Gross Heating Value, kcal/Nm^3	3420	2798
(Btu/SCF)	(384)	(314)
Elemental Analysis		
Wt % C	43.59	40.74
H	1.52	0.88
O (by difference)	54.89	58.38

Char was not produced from grass seed straw during this phase of the program.

Elemental Balances

From all of the foregoing data, elemental balances for each feedstock were made. For the cases of bark and rice hulls, closures on carbon, hydrogen and oxygen were calculated. This was done using the direct measurements of oil, water and gas yield, together with char and gas compositions. The char yield was obtained by difference. Two measures of the accuracy of these results are available: closure of the carbon and hydrogen balance, and comparison of the char yield by difference to the yield obtained from the direct heated char production runs. To the extent these statistics compare favorably, the overall validity of all the preceding results can be judged to fairly represent the reported yields and conversions.

For the case of straw pyrolysis, char compositions were not available as noted above. Here both the yield and the composition are generated by difference. The balances are given on a moisture-and-ash-free (MAF) feed basis. Only C, H, and O are reported since N & S in the gas were not measured. Also, oxygen is determined by difference and actually includes all other elements (including N & S). Since closure obviously could not be obtained for each run, all of the available yield and composition data for each feedstock have been averaged to smooth out the random variability. The table values can be traced item for item to the source data referenced previously. Details of the elemental composition data are presented at the end of this section (Tables II-20, II-21, and II-22).

The elemental balances support the overall validity of the results of this work. Closure of C, H, and O balances for tree bark are respectively 96%, 97% and 104%. Similarly, the closure for the rice hull runs is 99%, 100% and 100%.

The statistic char-yield-by-difference compares favorably to the results of the electrically heated char production runs. On an MAF basis, the by-difference char yield for bark is 22.4% vs the direct measured value of 22.3%.

Oil Moisture Analysis

Three methods were used in this work: azeotropic distillation using benzene or toluene and the titrimetric Karl Fischer (KF) method. The azeotropic method was chosen and used for all of the analyses so that the data would be internally consistent and comparable. This was done because the KF method could not be used to analyze samples obtained from isokinetic tests, the Brinks demister pad, or high moisture

Table II-5. ELEMENTAL BALANCE PYROLYSIS OF TREE BARK

(BASED ON MOISTURE-AND-ASH-FREE FEED)

	Yield, %	Composition, % C	H	O
Oil	39.8	60.1	6.0	33.9
Wax	3.0	78.5	13.1	8.4
Water	16.7		11.1	88.9
Gas	18.1	35.9	1.5	62.6
Char [a]	22.4	87.0	4.3	8.7
TOTAL [b]	100.0	52.3	5.9	41.2
Feed	100.0	54.3	6.1	39.6
% Closure		96	97	104

---

[a] Difference
[b] (Σ Yield x Composition) / 100

Table 11-10. ELEMENTAL BALANCE PYROLYSIS OF RICE HULLS

(BASED ON MOISTURE-AND-ASH-FREE FEED)

	Yield, %	Composition, %		
		C	H	O
Oil	30.2	62.24	6.11	31.65
Wax	0.0			
Water	26.6		11.1	88.9
Gas	7.3	37.72	0.70	61.57
Char[a]	35.9	75.84	4.74	19.42
TOTAL[b]	100.0	48.77	6.55	44.68
Feed	100.0	49.22	6.58	44.2
% Closure		99.1	99.5	101.1

---

[a] Difference

[b] (Σ Yield x Composition) / 100

Table [illegible]. ELEMENTAL BALANCE PYROLYSIS OF GRASS STRAW

(BASED ON MOISTURE-AND-ASH-FREE FEED)

	Yield, %	Composition, %			Weight (per 100 kg of feed)		
		C	H	O	C	H	O
Oil	33.3	61.9	6.4	31.7	20.6	2.1	10.5
Wax	2.1	78.5	13.1	8.4	1.6	0.2	0.1
Water	27.4		11.1	88.9	0.0	3.0	24.3
Gas	5.5	42.2	1.2	56.6	2.3	0.07	3.1
Char [a]	31.7	79.6	3.7	16.7	25.22	1.18	5.30
TOTAL	100.0	49.8	6.7	43.4			
Feed	100.0	49.8	6.7	43.4	49.8	6.7	43.5

---

[a] Char yield and composition by difference.

condensate samples. The KF method was thus useful only for primary oil samples obtained from the decanter tank (which represents 80% of the total oil yield). Also, the effect of moisture on oil yields is small, about 1-2% absolute on the oil yield result. The foregoing are all based on the benzene azeotropic method with the exception of the rice hull and straw isokinetic tests where toluene was used as the azeotropic solvent.

The overall effect of choosing the azeotropic method is to understate the oil yield somewhat since the product decomposes slightly to CO_2 and H_2O during the distillation process. Taking the KF method as being the more accurate, the benzene azeotropic method gives a high moisture result by a factor of 1.2, and the toluene azeotropic method a higher result by a factor of 1.6 (at an oil moisture content of 15%). The net result of this is to understate the oil yield by 1% absolute using benzene and 3-1/2% absolute using toluene. This has no effect on the C and H closures, as these in effect are based on the liquids (oil plus water) taken together.

PRODUCT TREATMENT AND PROPERTIES

Product Oil Properties

Table II-12 summarizes the pyrolytic oil properties for the product oils obtained from all three feedstocks (tree bark, rice hulls and grass straw). Figure II-3 shows the viscosity vs temperature behavior of the oils. Other properties and yield data are presented in previous tables in this section of the report.

Oil Treatment -

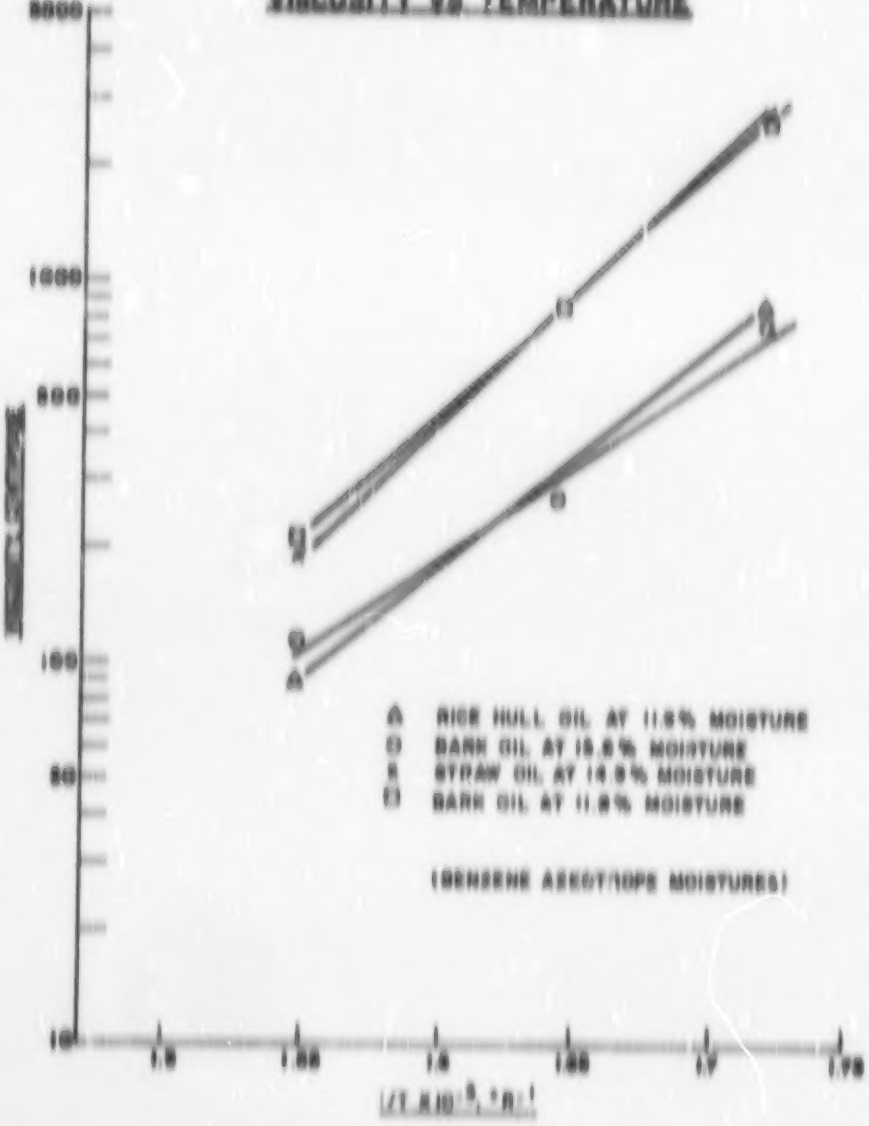
Filtration of the oil to remove char was generally not successful due primarily to the high viscosity of these oils. Tree bark oil from Run 53-73 was filtered more easily than oil from Runs 49-73 through 52-73. However, 100 micron pore size cloth was used and little char removal was accomplished in either case. Only one drum was completely filtered through 25 micron cloth, but it had a low char content initially. Typical results were:

Drum No.	Filter size (microns)	Tree Bark Oil Char Content, wt % Before	After
167	100	1.64	1.42
170	100	1.47	1.30
107	25	0.68	0.23
(167)	(25-Lab Test)	(1.42)	(0.48)

Table II-12. PYROLYTIC OIL PROPERTIES

Feedstock	Bark Lot I	Bark Lot II	Rice Hulls	Rice Hulls	Straw
Composition, wt %					
Quench Fluid	2.4	0.0	2.0	0.0	0.0
Char	1.1	1.2	3.3	1.9	3.5
Moisture (Karl Fischer)	13.49	9.50	11.96	---	---
Moisture (Benzene Azeo)	15.6	11.8	11.9	10.6	14.9
Specific Gravity, T/16°C (60°F)					
50°C (122°F)	1.254	1.266	1.230	---	1.243
64°C (148°F)	1.243	1.257	---	---	---
79°C (175°F)	1.232	1.244	1.200	---	1.200
Viscosity, centistokes					
50°C (122°F)	600 (2840SSF)	2000 (9400SSF)	660 (3170SSF)	--- ---	2100 (10010SSF)
64°C (148°F)	200 (990SSF)	630 (3000SSF)	--- ---	--- ---	--- ---
79°C (175°F)	92 (430SSF)	160 (770SSF)	66 (340SSF)	--- ---	150 (720SSF)
Pour Point, °C (°F)	21 (70)	24 (75)	7 (45)	--- ---	--- ---
Flash Point, (PMcc) °C (°F)	110+ (230+)	110+ (230+)	84 (184)	--- ---	--- ---
Heat of Combustion,					
$\frac{\text{cal}}{\text{gm}}$	5002	5193	5257	---	5529
(Btu/lb)	(8998)	(9341)	(9457)	---	(9945)
Ultimate Analysis, Wt %					
Moisture	13.49	9.50	11.96	---	7.0
Ash	0.66	0.74	2.32	---	1.91
C	60.36	62.57	53.43	---	55.46
H (dry basis)	6.90	6.67	6.38	---	6.65
N	0.27	0.32	0.69	---	1.24
S	0.03	0.04	0.06	---	0.09
Cl	0.03	0.02	0.04	---	0.07
O (by difference)	28.24	30.06	35.12	---	27.58

FIGURE II-5
PYROLYTIC OIL
VISCOSITY VS TEMPERATURE



A small quantity of the Drum 167 oil which had been passed through the 100 micron cloth was filtered through 25 micron cloth in the laboratory, but the cloth soon became blinded. Drum 167 could not be filtered through 25 micron cloth in the pilot plant under any circumstances.

Filtration of rice hull oil was even less successful than the tree bark product. Oil from Drum 525 was filtered first through 25 micron cloth and then 5 micron cloth. Typical results were:

Test	Filter Size (microns)	Rice Hull Oil Char Content, wt % Before	 After
1	25	3.24	3.16
2	5	3.16	3.23
3	5	3.23	3.19

Although this oil readily passed through even the small-pore 5 micron filter cloth, no char was removed. The general conclusion must therefore be that filtration is not an effective means of removing char from this type of oil.

An attempt was made to remove char from the oil using the pilot plant centrifuge, but a limiting value was found of about 1.5% char in the oil. The density of the small particles is apparently very close to that of the oil, so further reduction of char by centrifuging does not seem practical.

Decantation of the paraffinic quench fluid from the Lot I tree bark oil was only partially successful. After two hours of settling at 60°C (140°F) some of the quench fluid could be decanted, thus lowering its content in the oil from 3.7 to 3.4%. However, Lot II tree bark oil contained no quench fluid whatsoever.

Product Char

A summary of the char analyses is presented on Table II-13. Table II-14 summarizes the product char properties. Figures II-4 and II-5 present the measured screen analyses and particle size distribution, respectively. As expected, the char produced by direct heating has higher volatile matter content and lower ash than the char product after combustion tests. Bulk densities of all chars measured are about 0.19 gm/cc (12 lb/ft^3).

Water

A detailed analysis was made of the byproduct water collected in the total condensers in tree bark Run 53-73. About 14.5% of the sample collected was oil recoverable by distillation. The COD of this water phase was about 205 grams per liter, and pH was 3.6. A typical analysis of this water is:

Component	ppm	g/l
Na	7	
K	86	
Cl		0.04
Fe	6080	
Ca	8	
Mg	2	
Suspended Solids		0.11
COD		204.8

Table II-13. [illegible] ANALYSIS SUMMARY

	Tyler Mesh Screen Analysis (Cumulative % Retained)						Composition, wt %							
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	H_2O	Volatile Matter	Ash	C	H	N	S	O
[illegible]														
Run [illegible] (Original Char)*	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Run [illegible] (After combustion tests)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]														
Run [illegible] (Original Char)*	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Run [illegible] (After combustion tests)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Run [illegible] (Char and [illegible])	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Particle density, [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]								

*[illegible]

Table [illegible] [illegible] PROPERTIES

[illegible]		Run [illegible] – Original [illegible]	Run [illegible] – [illegible]	Run [illegible] – [illegible]	Run [illegible] – Original [illegible]	Run [illegible] – [illegible]
[illegible], wt %						
Volatile Matter		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ash		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] (by difference)		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]						
[illegible]		[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb	—
[illegible] *		[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb	[illegible] [illegible] Btu/lb
[illegible]						
[illegible]	[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	—	—	[illegible]
[illegible] kg/m^3		[illegible] ([illegible] lb/ft^3)	[illegible] ([illegible] lb/ft^3)	—	—	[illegible] ([illegible] lb/ft^3)

* [illegible] [illegible] [illegible] [illegible] [illegible]: Btu/lb = [illegible] [illegible] + [illegible] + [illegible] [illegible]

FIGURE II-4

BARK CHAR SCREEN ANALYSIS

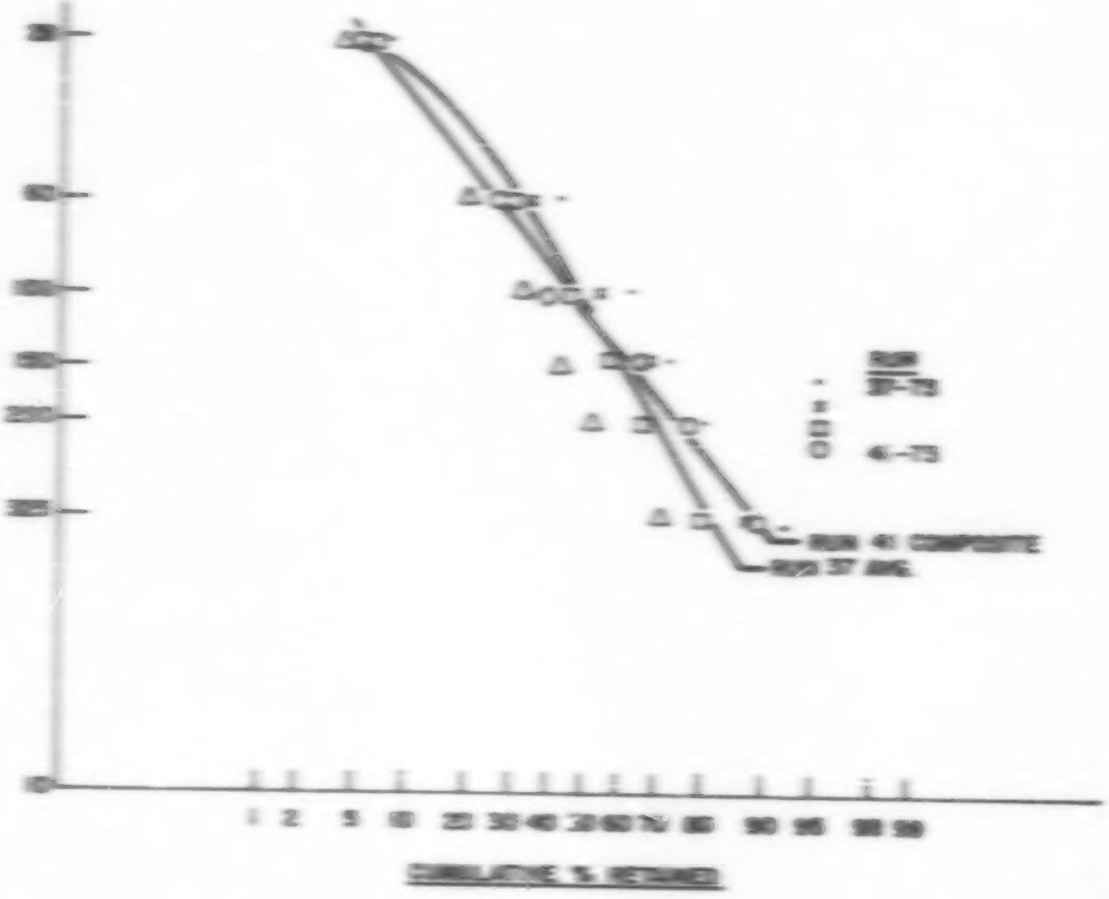


FIGURE II-4

FIGURE II-5

PARTICLE SIZE DISTRIBUTION

ELECTRICALLY PRODUCED TREE BARK CHAR—RUN 37-75

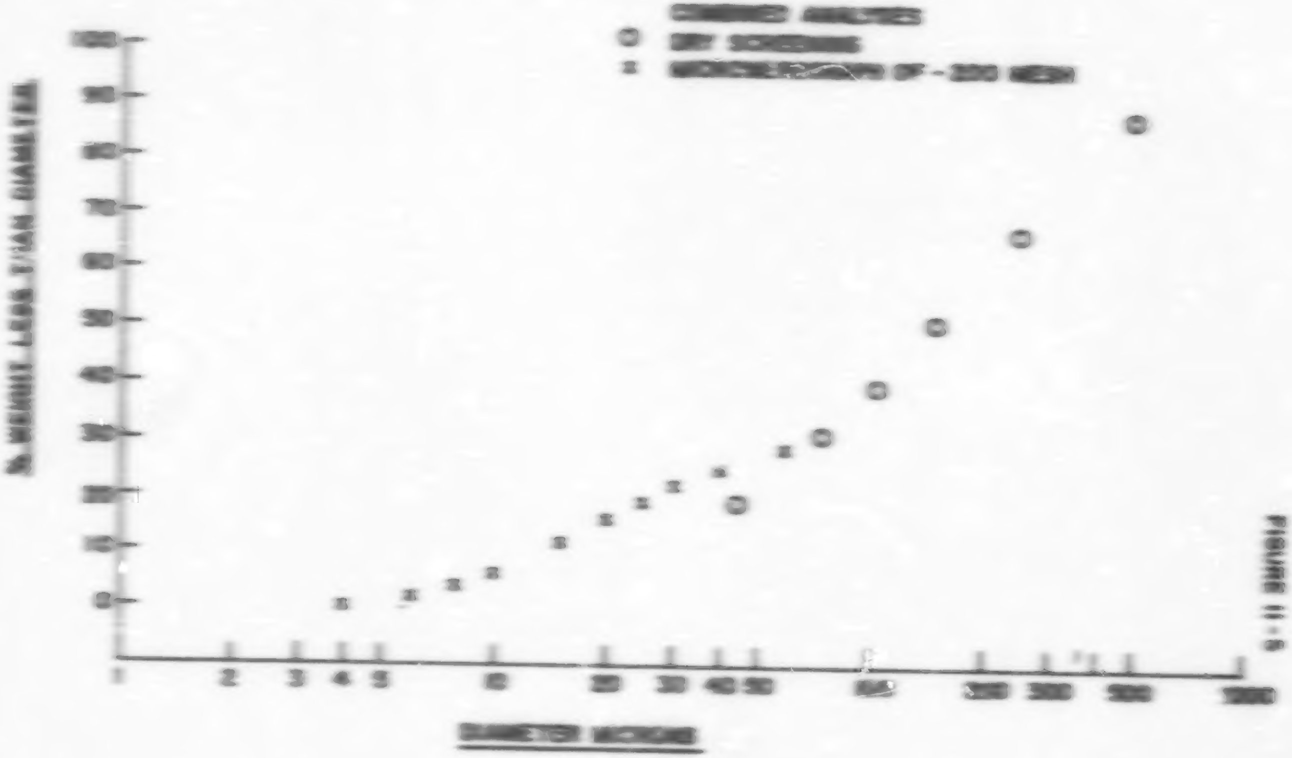


FIGURE II-5

Table II-15. SUMMARY OF LIQUID YIELD
TREE BARK - RUN 53-73

Weight of Feed:

	kg	lb
Dry	2218	4890
Moisture	109	240
As fed	2327	5130

Product Oil Yield (basis: dry feed)

Source	Weight, kg	Weight, lb	% of feed	% of yield
EP-101	662	1460	29.8	78.3
T-104 & Brinks Shell	94	208	4.2	11.1
Brinks Pads	30	66	1.4	3.6
Other	26	58	1.2	3.1
Vent Loss	33	73	1.5	3.9
TOTAL (Yield)	845	1865	38.1	100.0

Water Yield

Source	Weight, kg	Weight, lb
Product Oil Moisture	114	251
T-104 & Brinks Shell	252	556
Brinks Pads	15	33
Other	-	-
Vent Loss	68	150
TOTAL (recovery)	449	990
Less: Feed Moisture	(109)	(240)
Pyrolytic Water	340	750
Yield (basis: dry feed)	15.3%	

Quench Oil Inventory

	kg	lb
Charge,	1196	2637
Recovery,	1222	2695
Net Change,	+26	+58

Table II-16. SUMMARY OF LIQUID YIELD
RICE HULLS - RUN 83-71

Weight of Feed:

	kg.	lb.
Dry	1563	3446
Moisture	153	338
As Fed	1716	3784

Product Oil Yield (basis: dry feed)

Source	Weight, kg.	Weight, lb.	% of feed	% of yield
HP-101	300	661	19.2	73.8
T-104 & Brinks Shell	75	166	4.8	18.5
Brinks Pads	10	22	0.6	2.3
Other	-	-	-	-
Vent Loss	-	-	1.4	5.4
TOTAL (yield)	385	849	26.0	100.0

Water Yield

Source	Weight, kg.	Weight, lb.
Product Oil Moisture	61	135
T-104 & Brinks Shell	343	755
Brinks Pads	3	6
Other	-	-
Vent Loss	65	144
TOTAL (recovery)	472	1040
Less: Feed Moisture	(153)	(338)
Pyrolytic Water	319	702
Yield (basis: dry feed)	20.4%	

Quench Oil Inventory

	kg.	lb.
Charge	648	1428
Recovery	707	1559
Net Change,	+59	+131

Table II-17. SUMMARY OF LIQUID YIELD
RICE HULLS - RUN 84-7

Weight of Feed:

	kg.	lb.
Dry	1797	3963
Moisture	146	321
As Fed	1943	4284

Product Oil Yield (basis: dry feed)

Source	Weight, kg.	Weight, lb.	% of feed	% of yield
KP-101	329	724	18.3	72.3
T-104 & Brinks Shell	96	212	5.3	21.1
Brinks Pads	5	11	0.3	1.1
Other	-	-	-	-
Vent Loss	25	55	1.4	5.5
TOTAL (yield)	455	1002	25.3	100.0

Water Yield

Source	Weight, kg.	Weight, lb.
Product Oil Moisture	73	160
T-104 & Brinks Shell	404	890
Brinks Pads	6	14
Other	-	-
Vent Loss	41	91
TOTAL (recovery)	524	1155
Less: Feed Moisture	(146)	(321)
Pyrolytic Water	378	834
Yield (basis: dry feed)	21.0%	

Quench Oil Inventory

	kg.	lb.
Charge,	643	1418
Recovery,	594	1309
Net Change,	-49	-109

Table II-15. SUMMARY OF LIQUID YIELD

[illegible] RUN 65-73

Weight of Feed:

	kg.	lb.
Dry	2304	5080
Moisture	175	385
As fed	2479	5465

Product Oil Yield (basis: dry feed)

Source	Weight, kg.	Weight, lb.	% of feed	% of yield
KP-101	361	795	15.7	70.8
T-104 & Brinks Shell	116	255	5.0	22.7
Brinks Pads	-	-	-	-
Other	-	-	-	-
Vent Loss	33	73	1.4	6.5
TOTAL (yield)	510	1123	22.1	100.0

Water Yield

Source	Weight, kg.	Weight, lb.
Product Oil Moisture	76	168
T-104 & Brinks Shell	539	1188
Brinks Pads	-	-
Other	-	-
Vent Loss	75	166
TOTAL (recovery)	690	1522
Less: Feed Moisture	(175)	(385)
Pyrolytic Water	515	1137
Yield (basis: dry feed)	22.4%	

Quench Oil Inventory

	kg	lb.
Charge,	640	1410
Recovery,	596	1314
Net Change,	-44	-96

Table II-19. SUMMARY OF LIQUID YIELD
GRASS STRAW - RUN 66-74

Weight of Feed:

	kg.	lb.
Dry	1610	3550
Moisture	95	210
As Fed	1705	3760

Product Oil Yield (basis: dry feed)

Source	Weight, kg.	Weight, lb.	% of Feed
KF-101	331	731	20.6
T-104 & Brinks Shell	132	290	8.2
Brinks Pads	7	16	0.4
Other	-	-	-
Vent Loss	18	39	1.1
TOTAL (yield)	488	1075	30.3
AMSCO solubles	31	68	1.9
	519	1143	32.2

Water Yield

Source	Weight, kg.	Weight, lb.
Product Oil Moisture	58	129
T-104 & Brinks Shell	367	809
Brinks Pads	11	24
Other	-	-
Vent Loss	60	132
TOTAL (recovery)	496	1094
Less: Feed Moisture	(95)	(210)
Pyrolytic Water	401	884
Yield (basis: dry feed)	24.9%	

Quench Oil Inventory

	kg.	lb.
Charge,	513	1130
Recovery,	489	1078
Net Change,	-24	-52

Table II-20. SUMMARY OF COMPOSITION DATA
PYROLYSIS OF TREE BARK
(MOISTURE-AND-ASH-FREE)

	Run	C	H	O(diff)
Feed				
	AR 10/16/72	53.71	6.06	
	AR 5/17/73	54.07	6.22	
	53	53.42	6.01	
	53	55.90	6.13	
	Average	54.28	6.10	39.62
Oil				
	49 & 50	60.94	5.95	
	51	59.04	5.82	
	52	60.17	5.80	
	53	60.44	6.10	
	49 & 52	60.16	6.18	
	53	60.10	6.13	
	Average	60.14	6.10	33.76
Gas				
	53	36.35	1.71	
	53	35.54	1.24	
	Average	35.94	1.48	62.58
Char				
	37	92.83	4.75	
	37	93.98	4.90	
	37	86.66	4.31	
	37	84.18	3.92	
	38	85.25	4.30	
	41	78.92	3.78	
	Average	86.97	4.33	8.70

Table II-31. SUMMARY OF COMPOSITION DATA
PYROLYSIS OF RICE HULLS
(MOISTURE AND ASH-FREE)

FEED		MAF				
Run	Ash	C	H	N	S	O
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
66	20.11	49.03	6.02	0.57	0.71	44.00
AVG	19.47	49.22	6.10	0.60	0.08	43.80
67	18.20	56.19	6.34	0.63	0.23	36.81

CHAR			MAF				
Spl	Source	Ash	C	H	N	S	O
806	B101, T101	20.22	78.72	[illegible]	[illegible]	[illegible]	19.72
807		20.66	73.78	[illegible]	[illegible]	[illegible]	[illegible]
806, 810, 82 not analyzed							
872	B101 orig		78.34	[illegible]	[illegible]	[illegible]	[illegible]
876			76.46	[illegible]	[illegible]	[illegible]	[illegible]
AVG 806, 817			73.73	4.60	0.59	0.04	21.04
AVG all			75.84	4.74			19.42

Oil Analyses (MAF - Assu H_2O, not corr for char comp)

Run	Spl	H_2O	Ash	C	H	N	S	O
62	702	15.1	0.80	61.12	[illegible]	[illegible]	[illegible]	[illegible]
63	732	10.1	1.53	61.06	[illegible]	[illegible]	[illegible]	[illegible]
64	740	15.7	1.54	60.30	[illegible]	[illegible]	[illegible]	[illegible]
64	770	7.8	1.75	61.77	[illegible]	[illegible]	[illegible]	[illegible]
64	776	8.9	1.03	61.80	[illegible]	[illegible]	[illegible]	[illegible]
65	784	16.7	1.10	61.57	[illegible]	[illegible]	[illegible]	[illegible]
65	790	14.8	1.33	60.72	[illegible]	[illegible]	[illegible]	[illegible]
66	812	8.7	0.98	62.28	[illegible]	[illegible]	[illegible]	[illegible]
66	841	11.5	0.99	63.65	[illegible]	[illegible]	[illegible]	[illegible]
66	846	13.1	0.91	63.76	[illegible]	[illegible]	[illegible]	[illegible]
AVG all				62.34	6.11	0.90	0.08	30.67

Gas Analyses & Yield Summary

Test	Temp. °F	Yield	AHc	C	H	O
64-72-A	810	5.18	176	32.26	[illegible]	[illegible]
64-73-B	860	5.09	201	36.63	[illegible]	63.06
AVG (char heat)	840	5.34	198	34.44	0.38	65.17
65-72	900	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
65-73-F	910	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
67-74-A *	900	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
67-74-B *	950	6.00	361	41.46	1.63	57.01
AVG (char heat)	900	5.86	263	37.72	0.70	61.57
AVG all	900	5.49	290	38.66	0.91	60.43
65-72-B	950	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
66-73-B	950	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
67-73-A *	950	10.93	[illegible]	[illegible]	[illegible]	[illegible]
67-73-B *	960	6.30	[illegible]	[illegible]	[illegible]	[illegible]
AVG (char heat)	960	7.06	267	37.04	1.12	61.84
AVG all	950	8.59	304	39.06	1.40	60.53

NOTES: * Direct Heating

Table II-22. SUMMARY OF COMPOSITION DATA
PYROLYSIS OF GRASS STRAW
(MOISTURE-AND-ASH-FREE)

	C	H	O
Feed			
Run Composite	50.1	6.91	43.0
(replicate)	49.4	6.50	44.1
Average	49.8	6.7	43.5
Lab reactor data (Avg. of 3)	47.9	6.2	45.9
Oil			
Run Composite	61.9	6.4	31.7
Gas			
Run 66	43.59	1.52	54.89
Run 66	40.74	0.88	58.38
Average	42.16	1.20	56.64

SECTION VI

PHASE III - PRODUCT EVALUATION

INTRODUCTION

This section presents the results of the product evaluation studies (Phase III) using the pyrolytic char and oil products generated during the pilot plant studies (Phase II).

Converting solid waste materials to liquid fuel is intended to make it possible to conveniently store and transport the combustible portion of the waste while reducing its ash content, and to be able to fire it using conventional fuel-oil-firing equipment. The KVB Company, Inc. of Tustin, California was hired under subcontract to conduct combustion tests to determine flame stability and pollutant emissions of the pyrolytic oils from tree bark and rice hulls relevant to their use as fuels in industrial and utility boilers. The results of the tests were favorable and show that pyrolytic oils can be successfully used as a substitute or supplement to the residual petroleum-based oils typically used in commercial fuel oil firing equipment.

The byproduct char samples were evaluated for use as barbecue briquettes and as a raw material for the manufacture of activated carbon. The Royal Oak Charcoal Division of Georgia Pacific Corporation contributed studies in association with this program on two lots of Douglas fir bark char and concluded that this material is suitable for the manufacture of good quality barbecue briquettes provided the volatile matter content is kept below about 15%.

The St. Regis Paper Company was hired under subcontract to evaluate the suitability of bark and rice hull char for making activated carbon. The St. Regis equipment was unfortunatley not capable of handling and pelletizing the fine char at commercially feasible levels of binder concentrations.

Nevertheless, the results indicate that char could be activated with some difficulty even under these conditions and that a modestly attractive throw-away, powdered activated carbon could probably be produced. It was also found that the rice product was too high in ash to produce an acceptable activated product. In order to verify these conclusions, however, further tests would have to be conducted employing equipment designed to handle this finely divided material.

PRODUCT PREPARATION

Pyrolytic Oil

Preparation of the bark and rice oils shipped to KVB for combustion testing was discussed in some detail in Section V of this report (Pilot Plant Studies). These steps consisted of filtering and centrifuging the oil for char removal and decanting the oil to separate any carry-over quench fluid. A summary of the properties of the tree bark oil shipped to KVB is presented on Table III-1.

Table III-2 shows a comparison of the properties of rice hull oil - Lot 1 as measured by both Garrett and KVB. The only substantial difference is in the measured moisture content of the oil. The differences among moisture contents obtained by using different analytical techniques were discussed in the previous section. The Toluene Azeotropic Distillation Method used by KVB suffers from systematic errors when applied to pyrolytic oils as discussed earlier. The oil analyzed by Garrett shows about 12% water by the Karl Fischer Method and this is within the range to be expected compared to KVB's results.

Conditioning of Pyrolytic Char

The starting material for activation studies by the St. Regis Paper Company was the tree bark char produced by direct heating in Run 37-73. The material was originally to have been sent directly to St. Regis, but because of the high volatile matter (VM) content of 23.03%, further devolatilization in the pilot plant was necessary. Two batches were processed, with reactor gas temperatures being approximately 93°C (200°F) higher for the second batch. Product weights of 4.6 kg (10.14 lb) (9.62% VM) and 6.6 kg (14.48 lb) (3.87% VM) resulted. Samples of 0.3 kg each of original char (23.03% VM), Batch 1 product (9.62% VM), and Batch 2 product (3.87% VM) were shipped to St. Regis.

Table III-3 presents an analysis of the Run 37-73 char before screening or devolatilization, and includes a summary of devolatilization conditions and results.

Table III-1. PROPERTIES OF BARK OIL SHIPPED TO KVB ENGINEERING FOR COMBUSTION TESTING

LOT	I		II	
Pilot Plant Runs	49, 50, 51, 52		53	
Net weight, kg	821		603	
Composition, wt %				
Moisture	17.0		13.3	
Quench Fluid	2.4		0.0	
Char	1.1		1.2	
Specific gravity, T/16°C (60°F)				
50°C (122°F)	1.254		1.266	
64°C (148°F)	1.243		1.255	
79°C (175°F)	1.232		1.244	
Viscosity	SFS	Cp	SFS	Cp
50°C (122°F)	284	753	940	2500
64°C (148°F)	99	260	300	800
79°C (175°F)	42	105	77	200
Pour point	21°C (70°F)		24°C (75°F)	
Flash Point (P.M.c.c.)	110+°C (230+°F)		110+°C (230+°F)	

Table III-2. COMPARISON OF PYROLYTIC OIL PROPERTIES MEASURED BY GARRETT AND KVB

RICE HULL OIL - LOT 1

	Garrett Analysis	KVB Analysis
Ultimate Analysis, wt %		
Moisture	11.86[a]	19.52[b]
Ash	2.32	2.36
C	53.61	55.27
H (excl. H_2O)	6.16	4.73
N	0.69	0.78
S	0.06	0.08
Viscosity, Centistokes		
77°C (170°F)	-	140 (650 SSU)
79°C (175°F)	90 (420SSU)	-
Flash Point	84°C (184°F)	104°C (223°F)
Heat of Combustion	5250 cal/gm (9457 Btu/lb)	5400 cal/gm (9723 Btu/lb)

[a] Karl Fischer titration

[b] Toluene azeotrope distillation

Table III-1. PROPERTIES AND DEVOLATILIZATION CONDITIONS FOR BARK CHAR SENT TO ST. REGIS PAPER COMPANY

Analysis of Bark Char 37-[illegible]

Component	C	H	N	S	Ash	O (Diff.)	Higher Heating Val.	Volatile Matter
Wt % (dry basis)	68.80	2.40	0.27	0.08	26.45	1.62	[illegible]	21.83

Devolatilization Conditions

	1	2
Wt feed ent., kg	6.6	6.5
Wt product, kg	4.6 (10.14 lb)	4.5 (10.40 lb)
Devolatilization losses, wt %	30.1	30.1
Run Duration, minutes	187.	200.
Feed		
-20 mesh Bark Char from Run 37-[illegible] Init. VM, before screening	21.5%	21.8%
Transport gas		
Gas Flow Rate (Preheater/Transport)	2.5/1.3 SCFM	2.5/1.7 SCFM
Gas Residence Time per cycle (Reactor Inlet to Cyclone #1 exit)	0.5 sec	0.5 sec
Temperatures, °C		
Preheater Exit Gas	816(1500°F)	871(1600°F)
Reactor Inlet Gas	482(900°F)	482(900°F)
Reactor Exit Gas	760(1400°F)	871-899(1600-1650°F)
Cyclone #1 Inlet Gas	704(1300°F)	816(1500°F)
Feed Rate, kg/hr	2.31(5.07 lb/hr)	2.23(4.91 lb/hr)
Cyclone Efficiencies (Basis: product)		
Cyclone #1	67.4	66.1
Combined (three cyclones)	92.6	92.5
Pressure, Reactor Inlet, atm	<0.1(<1.5 psig)	<0.1(<1.5 psig)
Char volatile matter (cyclone #1), wt %	9.62	2.57

OIL EVALUATION

Combustion tests were conducted by KVB, Inc. on two lots of tree bark oil and two lots of rice hull oil described in Tables III-1 and III-2 respectively. A detailed description of the test conditions and results of these tests is given in a report from KVB to Garrett which is included in the Appendix (Section IX of this report). The objective of the KVB tests was to determine flame stability and pollutant emissions of the pyrolytic oils relevant to their use as fuels in industrial and utility boilers. The KVB test results are summarized below and other details from earlier tests are given in Reference 2.

Pyrolytic oils were found to be suitable fuels for a large power station boiler with a properly designed storage and handling system. Some of the differences of pyrolytic oils from the heavy residual oils commonly used in utility boilers are:

1. They are water-based and therefore are immiscible with petroleum-derived oils. (They can, however, be blended as a binary dispersion with most types of residual fuel oils).

2. They are slightly corrosive because they contain acetic acid as well as other organic acids; therefore, they require additional consideration in shipping, storage, pumping, and plumbing.

3. They are heat-sensitive. Although moisture content can be controlled in the production process to give a viscosity-temperature relationship similar to that of residual oil, the preheating which is necessary to bring the fuels to firing viscosity (100-200 SSU), if not done carefully, can cause irreversible changes in physical properties. In addition, the viscosity is not a function of temperature alone, but of the temperature-time history of the pyrolytic oil. Thus the liquid's properties can change over a long storage period at elevated temperature.

4. A lower heat content, 25 to 30% less than that of a similar volume of residual oil, requires greater fuel pumping and storage capacity for a given heating rate.

Typical properties of No. 6 fuel oil and pyrolytic oils are shown in Table III-4.

Table III-4. TYPICAL PROPERTIES OF NO. 6 FUEL OIL AND PYROLYTIC OIL

	No. 6	Pyrolytic Oil
Carbon, wt % (dry basis)	85.7	57.5
Hydrogen	10.5	7.6
Sulfur	0.5 - 3.5	0.1 - 0.3
Chlorine	-	0.3
Ash	0.5	0.2 - 0.4
Nitrogen Oxygen	2.0	0.9 33.4
Btu/pound	18,200	10,500
Sp.Gr.	0.98	1.30
Lb/gallon	8.18	10.85
Btu/gallon	148,840	113,910
Pour Point °F	65 - 85	90[a]
Flash Point °F	150	133[a]
Viscosity SSU @ 190°F	90 - 250	1,000[a]
Pumping temperature °F	115	160[a]
Atomization temperature °F	220	240[a]

[a] Oil contains 14 wt % H_2O

Tree Bark Oil

Petroleum-derived residual oil was used to fire the KVB test boiler for cold starts and to purge the boiler for the last ten to fifteen minutes of firing on each day's testing on tree bark oil. Lot 1 was burned satisfactorily for several minutes at a time, but trouble was encountered due to repeated plugging of the atomizers by char particles present in the oil. While larger diameter atomizer orifices in a commercial scale boiler might not have plugged, these smaller scale tests reveal the need for a complete range of standardized inspection tests for pyrolytic oils similar to the common tests used on petroleum-derived oils.

The remainder of the tree bark oil tests were made using the Lot 2 oil. With the ignitor on, the tree bark oil burned stably over a wide range of conditions. Operation without sustained use of the ignitor might have been possible if there had been enough pyrolytic fuel to enable variations in burner settings. Ignitor fuel consumption was small: less than two percent of the total heat input.

After a shutdown of several seconds to five minutes, the burner could be restarted on tree bark oil without using residual oil. No attempt was made to start up on tree bark oil with a cold furnace, but this was satisfactorily accomplished later with pyrolytic rice hull oil.

Changes from one fuel to the other were made gradually over a period of several minutes, so that a wide range of mixtures of tree bark oil and residual oil were burned. No difficulty was encountered in burning these mixtures.

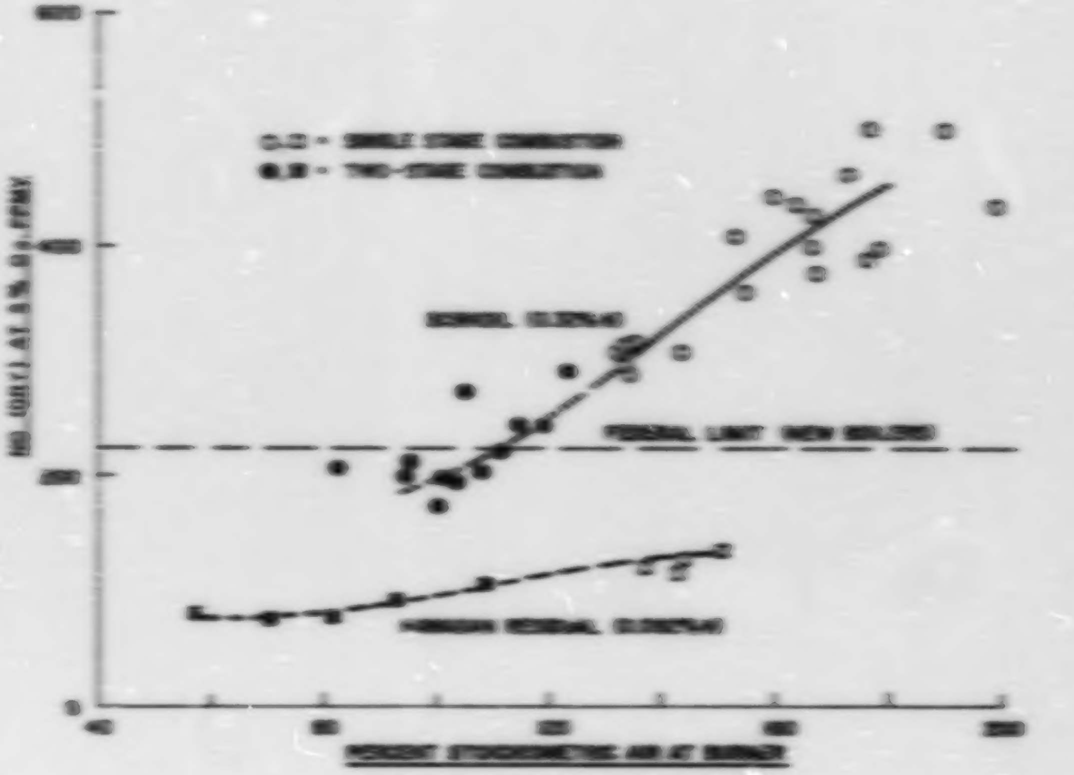
For all the test points on this batch of tree bark oil, the firing rate was approximately 360,000 Kcal/hr (1,500,000 Btu/hr). A total of seven hours of running time was accumulated firing 100% pyrolytic oil. Carbon monoxide concentrations on a dry basis were below 50 ppm (volume) for all points, and at normal excess air levels, there was no visible smoke except for a very light plume (about 10% density) which occurred at a few conditions. However, moving the diffuser and gun 1.3cm (1/2 in.) farther into the fire box eliminated the smoke. Combustion was stable and smokeless as excess oxygen was increased from 2.5% to 9.4% with a tree bark oil temperature of 91°C(196°F).

The tree bark oil burned well with two-stage combustion, a widely-used technique for reducing nitric oxide formation in large boilers. Figure III-1 shows nitric oxide concentration in the flue gases vs A_B, the percent of stoichiometric air flow through the burner. Each curve has two sections.

FIGURE III-1

FIGURE III-1

CORRECTED NITRIC OXIDE CONCENTRATION VS. BURNER AIR FLOW



The open symbols represent single-stage combustion; that is, all the air flows through the burner. The solid symbols represent two-stage combustion wherein part of the air flows through the burner and the remainder enters the furnace farther downstream through the second-stage air torus. The overall combustion air flow was as low as 117% of stoichiometric for several of these points.

For the Lot 2 tests, a low-nitrogen No. 5 residual oil from a Hawaiian refinery was used for startup and post-run fuel system purges. Nitric oxide data for this oil are also shown in Figure III-1. An analysis of the oil is given in the KVB report in the Appendix.

For both oils, two-stage combustion results in less nitric oxide emission. The original data sheets are also reproduced in the KVB report in the Appendix. Typical test data for tree bark oil and the Hawaiian residual oil are given in Table III-5. No changes in burner configuration were made in changing from one fuel to the other.

Rice Hull Oil

The fuel derived from rice hulls was also supplied in two batches. Complete analyses are given in Table III-2. The water analyses are believed inaccurate as discussed above due to the Toluene Azeotrope Method used to determine moisture content. Corrected values of C, H, and O were used in determining flue gas O_2 vs excess air for this oil. This particular calculation is not very sensitive to fuel composition.

Lot 1 -

Initially, attempts were made to fire Lot 1 under exactly the same conditions which were successful with the Lot 2 tree bark oil. However, these were unsuccessful due to repeated internal blockage of the atomizer. Subsequent testing was carried out using Lot 2 with very little difficulty.

Lot 2 -

There was a visible difference between Lots 1 and 2 for both the tree bark oil and the rice hull oil. In both cases Lot 2 was more viscous and had a creamy texture, while Lot 1 was more watery in texture. Rice hull oil Lot 2 seemed to have much less tendency toward atomizer blockage and thus was fired successfully despite its higher viscosity.

Table III-5. TYPICAL OIL COMBUSTION TEST DATA

Fuel	[illegible]	[illegible]	Tree Bark Oil	Tree Bark Oil
Test Description	Single-stage	Two-stage	Single-stage	Two-stage
Duration, minutes	45	6	45	4
Pressures				
Windbox, mmHg	1.12	0.28	1.03	0.28
Fuel, atmg	3.4	3.4	4.9	3.6
Steam at gun, atmg	3.4	3.5	4.8	3.7
Temperature				
Fuel, °C	93	72	89	93
Steam at rotameter, °C	174	174	174	174
Windbox air, °C	159	160	161	164
Combustion chamber, exit, °C	593	588	641	626
Stack gas at inlet, °C	190	182	199	188
Flows				
Atomizing steam, kg/hr	6.8	8.2	17	8.2
Fuel, kg/hr (from O_2)			75	69
Total air, kg/hr	725	665	727	664
Total air, percent of stoichiometric (from O_2)	138	117	141	140
Burner air, percent of stoichiometric	138	73	140	75
Concentrations				
Excess oxygen (dry), percent	5.8	3.2	6.1	6.1
NO (dry) corrected to 3% O_2	133	90	402	165
Smoke density (visual), %	0	0	1	0
SO_2, ppm	211	a	28	a
SO_3, ppm	1.7	a	0.5	4
CO, ppm	15	25	30	6

[a] Not measured

In order to minimize thermal alteration of the rice hull oil, the interim storage drum temperature was kept low, 54°C (130°F) and atomizing steam boiler pressure was kept as low as was practical, 6.4 atm (80 psi at the rotameter). The steam mass flow rates varied from 10 to 20% of the fuel flow rate. Steam pressure at the gun was approximately 4.7 atm (55 psi) for most points and oil pressure was within 0.7 atm (10 psi) of steam pressure.

The first runs using Lot 2 were made using combustion air at 104°C (220°F) and 168°C (335°F), with the ignitor on. Successful cold-furnace startups were also made using only rice hull oil fuel. The first firing lasted 1 hour 27 minutes before shutdown became necessary due to marked deterioration of the spray.

In the next firing, clinker buildup on the diffuser occurred. This was eliminated by moving the oil gun tip 1 cm (1/2 in.) farther into the furnace so that the tip was flush with the downstream face of the diffuser. Because of this change the rest of the rice hull oil runs are not strictly comparable to the tree bark oil runs.

In all, the rice hull oil runs covered a range of 176,000 Kcal/hr to 503,000 Kcal/hr (700,000 to 2,000,000 Btu/hr) in heat input rate. Carbon monoxide emissions were below 100 ppm at excess oxygen levels from 1% to 10%. There appeared to be no unburned carbon emissions in this range. Staged combustion at 3% excess oxygen resulted in nitric oxide levels of 200 to 400 ppm. Use of the ignitor was not necessary to sustain the flame.

Conclusions

1. In general it can be said that the pyrolytic oils gave satisfactory performance in the combustion tests. It must be stressed that the pyrolytic oil is not interchangeable with distillate or residual oils in most boiler installations without modifications to storage and pumping facilities. This is due to several properties of the pyrolytic oils which were mentioned previously; they are acidic; their properties are fairly easily changed by overheating; their properties change if the oils are allowed to evaporate at firing temperature for appreciable lengths of time; and they can form deposits on valves and heating surfaces if the system is not properly designed. However, the system changes necessary to accomodate pyrolytic oils may not be more difficult than, say, the changes needed to accomodate No. 6 heating oil in a system designed for No. 2 oil.

2. The pyrolytic oils appeared to be compatible (i.e. could be blended) with most residual fuel oils representing different geographical sources. However, the residual oils did not completely purge the fuel system of pyrolytic oils.

3. The most likely initial problems encountered by pyrolytic oil users would be in quality control, storage, pumping, and atomizer blockage. Users should run thorough pumping and atomizing tests before attempting to fire these oils. Fuel specifications should restrict suspended solids, gum formation, heating value changes, viscosity changes, and other variations which are possible in any fuel oil, or which may in some cases be peculiar to pyrolytic oils.

4. It appears possible that when firing pyrolytic fuels the Federal NOx limitations on new units can be met by using staged combustion, although perhaps without much margin.

5. The pyrolytic oils tested had such low sulfur content that no problems due to sulfur oxide corrosion or sulfur oxide emissions are anticipated from this oil.

6. Stack gas cleanup would be required to meet EPA particulate regulations in the oils tested.

CHAR EVALUATION

Tests were made on several lots of Douglas fir bark char to determine its suitability as charcoal briquettes, or as a raw material for activated carbon. Char preparation was discussed above.

Charcoal Briquettes

Two lots of 4.5 kg (10 lbs) each of tree bark char were sent to the Royal Oak Charcoal Company (a Division of Georgia-Pacific Corporation) having the following characteristics:

	Lot 1	Lot 2
Volatile Matter, wt %	24.0	7.4
Ash, wt %	9.4	[illegible].2

Briquettes were made on a laboratory press and the test results are summarized below.

Lot 1 -

The high volatile matter content of this lot caused the char to be very spongy. The material required a large percentage of starch to bind it into briquettes, and the resulting briquettes developed large cracks upon drying with a generally bad appearance. In addition, the burning briquettes smoked vigorously and emitted a disagreeable odor. Lot 1 char was thus judged not to be suitable for barbecue briquettes.

Lot 2 -

This char briquetted very well with substantially less starch binder and dried firmly without cracking. The briquettes ignited and burned well without any disagreeable odor and produced a typical grayish-brown ash.

The Lot 2 char is considered to be suitable for manufacturing good quality barbecue briquettes. Royal Oak estimated that the volatile matter content might be as high as 15% and still have the desired properties to make a good quality barbecue briquette.

The report from Royal Oak Charcoal Company is included in the Appendix (Section IX) of this report.

Tree Bark Char Activation

Three samples of Douglas fir bark char were sent to the St. Regis Paper Company for evaluation as a potential raw material for activated carbon. The properties of these samples are given on Table III-3, and the preparation of the samples was described above.

Preliminary Evaluation -

The three samples were shipped for prescreening and the most suitable for activation was chosen for further study. Of these three materials, the best prospect for activated carbon was that which, by a Garrett determination, contained 8.62% volatiles. Following St. Regis' procedures for volatile determination, the data did not correspond to that supplied by Garrett. However, duplication of Garrett's technique by St. Regis yielded very similar results. The ASTM procedure followed by Garrett can yield low values for volatile matter if these volatiles are driven off very slowly. Both Garrett and St. Regis agreed that the method used by St. Regis gives a value which is more meaningful in evaluating the chars' potential for activation. The moisture, volatile matter, ash content, reaction rate in an activating medium, nitrogen and carbon dioxide surface areas were measured, and the results are given in Table III-6.

Table III-4. [illegible]

Material [illegible]	[illegible]			Reactivity		Surface Area	
[illegible]	% [illegible]	% Volatiles[a]	% [illegible]	Gas	[illegible]	N_2 Area	CO_2 Area
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[a] Determined with [illegible] as a final temperature.

The data indicated the three chars had similar volatile matter, ash content, and reactivity. Inspection of the laboratory data showed a larger amount of volatile matter given off below 600°C for the 9.62% sample over the 3.07% sample, although the total volatile matter was nearly the same at 850°C. As some preliminary pore development takes place by volatilisation of material below 600°C, this factor indicated the 9.62% material might be more suitable for activated carbon than the 3.07% material. The 23.03% volatile material appeared under microscopic study to be in the form of only slightly charred wood or bark. There would probably be little, if any, advantage in working with this material in relation to beginning with totally untreated raw tree bark. The determination of nitrogen and carbon dioxide surface areas finally demonstrated that the 9.62% material was the most desirable. The differences between the nitrogen and carbon dioxide areas gives a qualitative indication of the micropore structure which may be utilised in further activation. This difference was 160 m^2/gm for the 9.62% material, the highest of the group.

Upon being informed of St. Regis' decision to use the so-called 9.62% material for further work, Garrett Research provided two additional samples of this material, and these were blended by St. Regis with the original to ensure uniformity.

Compaction Studies -

Preliminary compaction work using coal tar pitch as a binder and a pellet press at various temperatures, pressures, and binder concentrations proved unsuccessful. Consultation with and experimentation by K.G. Industries in Chicago substantiated these findings. A liquid phase binder, particularly lignosulfonate pitch, was suggested. Work at St. Regis showed that the lignosulfonate pitch solution would pelletise, cure to a strong pellet, and withstand carbonisation without deterioration. However, the carbonised binder is much more reactive than the base char and under mild activation conditions would burn off leaving the char powder unsupported by a binder matrix.

The above results pointed to the necessity of developing a low reactivity binder system with high strength. Toward this end, two coal tar pitch dispersions were made. The first was a blend of octanol and coal tar pitch and the other was an octanol-acetone solution with coal tar pitch added. Pellets produced from octanol and pitch alone proved to be the strongest after carbonisation and these were activated under the same conditions as the protein bound pellets. There was some deterioration of the pellets, but considerably less than experienced when using the protein colloid or the lignosulfonate.

These studies are described in more detail in a report to Garrett from the St. Regis Paper Company which is included in the Appendix (Section IX).

Conclusions -

Nitrogen surface area measurements were made on the octanol-pitch bound char and the lignosulfonate bound char, both activated at 11% CO_2 at 750°C for two hours. These surface areas were 254 m^2/g and 336 m^2/g for the octanol-pitch and lignosulfonate bound material respectively. It appears that the octanol may hinder pore development. This is possible, as the octanol may be able to be trapped by the char's pores and, if unable to volatilise rapidly out of the system, will carbonise in place, plugging the pores and thus hindering further surface area development.

Coal tar pitch and lignosulfonates are both inexpensive materials, i.e., approximately 8 and 5 cents/lb respectively. A protein colloid binder would be economically feasible, commercially, only at very low binder levels, as the cost is approximately 40 cents/lb. Organic dispersants such as octanol are quite expensive and would probably require a solvent recovery system if used in large quantities.

Even the unactivated char has a high ash content. Thus, activation at even a moderate burn off would yield a carbon with a very high ash. Acid washing of the char to lessen ash content could be beneficial for activation. The fact that ash content can affect binder efficiency and thus final product strength also points toward the need for study in this area. Through activation of pelletised Garrett material, nitrogen surface areas of 250 and 340 m^2/gm were obtained, based on total material. On an ash free basis the area is 360 to 480 m^2/gm carbon.

No optimisation to obtain the minimal binder level for tree bark char was performed. Binder levels of 22% in general are too high for commercialisation. A typical commercial binder concentration is 6% but attempts to pelletise at this level were unsuccessful. If the Garrett char production system were revamped to permit granular material to be formed, the necessity for compaction could possibly be eliminated. Unless a suitable binder system is developed, Garrett tree bark char as supplied may be utilised only as a source of raw material for powdered activated carbon. Its low density would make activation as a powder difficult.

Rice Hull Char Activation

Activation tests on rice hull char were conducted subsequent to the work on the tree bark product. While the rice hull material was considerably easier to compact, the very high ash content of approximately 60% is generally believed to preclude its acceptance in its delivered state as a source material for activation. St. Regis reports that due to this high ash content, quantitative atomic absorption analyses on this material were not conducted. However, the high surface area of the available carbon in the raw rice hull char was believed to be quite suitable for activation, if further processing steps could be employed to lower the ash level. Some acid leaching may look promising, but further work, outside the scope of this program, would have to be undertaken before this product could be considered as a suitable source of activated charcoal.

The St. Regis report, covering details of their work on rice hull char, is included in the Appendix (Section IV) to this report.

SECTION VII

PHASE IV - ECONOMIC FEASIBILITY STUDY AND PRELIMINARY PROCESS DESIGN FOR TREE BARK PYROLYSIS

INTRODUCTION

The final section of this report presents the results of Phase IV - an engineering process design and economic evaluation of the Garrett Flash Pyrolysis process for the conversion of Douglas fir bark to synthetic fuel oil and saleable char products. The design calculations and cost estimates are prepared for two commercial size plants using the pilot plant data described above in Phase II, and the evaluation of the oil and char as marketable products described in Phase III.

The two sizes considered are 300 and 1200 Tons per day (272 and 1089 metric tons per day) pyrolysis plants (on an oven dry basis). Products are a low sulfur barkoil suitable for use as a utility boiler fuel or as a blend with NO. 6 fuel oil in a utility boiler; and char which is marketable as a fuel, as charcoal briquettes or as a source of inexpensive, powdered, throw-away activated carbon.

The economic evaluation indicates that a commercial plant sized to process 300 Tons per day (dry) of tree bark will essentially break even assuming the char is sold as briquettes. A 1200 Ton per day plant, however, shows a fair return on investment, even if only the oil is sold.

DESIGN BASIS

Table IV-1 presents the design basis and operating conditions for the plant.

Table IV-1. DESIGN BASIS

Feed: Tree Bark	= 45 wt. % Moisture
Primary Shredder	= 16 hrs/day - 7 days/wk 80 -8cm (-3")
Air Classifier	= -8cm (-3") Overhead, 45% Moisture +8cm (+3") Recycle to primary shredder.
Secondary Shredder - Drier	= 24 hrs/day - 7 days/wk 90% -24 mesh, 5% Moisture
Bark Consumed as Drier Fuel	= (5 wt % of feed, maximum (dry basis))

Pyrolysis Yields at 510°C (950°F)

	Wt % of dry Pyrolysis feed
Oil	37
Wax	3
Gas	17
Water	15
Char	28
	100

Gas	(Mole %)
H_2	10.0
CO	36.0
CO_2	46.2
C_2H_4	5.4
C_2H_6	0.6
C_3H_6	0.9
C_{4+}	0.9
	100.0

HHV = 1.04×10^7 J/std m^3 (280 Btu/SCF)

MW = 32.5

Table IV-1. DESIGN BASIS (cont.)

Pyrolysis (cont.)	Barkoil Sp Gr @ 80°C(175°F) = 1.24 VISC, CP @ 80°C(175°F) = 200 HHV (DRY) = 5830 cal/g (10,500 Btu/lb)	
Liquid Collection Train	15 wt % H_2O in Barkoil 5 wt % Barkoil in Quench 10 wt % Wax in Quench 1 wt % Quench in Barkoil Decanter Res. Time=10 min.	
Liquid Storage	Tank	Storage Capacity
	Rundown	8 hours
	Off Spec	1 day
	Product Storage	3 days
	Quench Storage	Volume of Quench System
Cost Basis	February, 1974 costs 20-year plant life Site is clear and level	

An economic evaluation is given for two feed rates; 300 Tons per day and 1200 tons per day, on an oven dry basis. These rates correspond to 545 tons per day and 2182 tons per day wet tree bark, respectively, having an average moisture content of 45 weight percent water. The plant is designed to process the bark at these rates, seven days per week, 350 days per year. Primary shredders are sized to operate 16 hours per day followed by sufficient storage capacity to permit the rest of the plant to operate 24 hours per day at the design rates.

Marketable products are barkoil and pyrolytic char. The wax produced is of a low quality, and for purposes of this feasibility study, it is assumed that the wax cannot be economically recovered at the purity required by the market. All the gas produced is consumed in the process as transport recycle and fuel gas. In addition, a small amount of the dry shredded bark may be needed as fuel in the Secondary Shredder - Drier (less than 5%).

The pyrolysis reactor operates at about 1 atmg (15 psig) and 510°C (950°F). The liquid collection train decanter is designed to operate at 0.34 atmg (5 psig) and 80°C (175°F). Pressure balances on the fluidised char beds have not been calculated, but the 0.68 atm (10 psi) drop allowed in the design is sufficient to meet the requirements in the pyrolysis area.

No special flexibility or redundancy is included in the design. Spare equipment is provided only where dictated by process considerations (e.g. spare pumps for the quench and barkoil from the decanter in the liquid collection train to guard against upset conditions in the pyrolysis area). Plant capacity is basically limited by the capacity and operation of the primary and secondary shredders.

The economic analysis is based on February 1974, equipment costs. Operating labor and utilities costs are also based on February 1974 levels. It is assumed that the site is clear and level, and that the plant would have a useful life of 20 years. The cost of the land is not included.

PROCESS FLOW

Figure IV-1 presents the process flow diagram and material balance for the plant.

Tree bark from the receiving area is loaded onto a system of conveyors which carry the material to the Primary Shredder. Primary shredding reduces the size of the bark to less than 8 cm (3 inches). The shredded bark is conveyed to interim storage providing 8 hours surge capacity. The shredded bark, still at 45 weight percent moisture, is essentially dust free.

Shredded bark from the Storage Bin is conveyed to the Air Classifier which separates the bark less than 8 cm (3 inches) into an overhead stream, passing through the Air Classifier Cyclone to the Packaged Secondary Shredder-Drier System from the bark greater than 8 cm (3 inches) into a bottoms stream which is screened to remove inorganics and recycled to the Primary Shredder.

The Packaged Secondary Shredder-Drier System receives the 8 cm (3 inch) and smaller bark from the Air Classifier. This system introduces the raw material into a grinding chamber along with hot inert gas. Particle size is reduced to 80% less than 24 mesh and simultaneously dried to 5 weight percent moisture. The finely shredded, dried bark is fed to a secondary surge system, which has 8 hours capacity, so that upsets or maintenance requirements in the shredding system will not interrupt operation in the pyrolysis area.

A screw feeder conveys a measured amount of dried, shredded bark to the Reactor, lifted by transport gas and combined with hot 760°C (1400°F) circulating char. Flash pyrolysis occurs in the reactor at 510°C (950°F) to convert the bark into bark oil, char, wax, and pyrolysis gases. Char is separated from the reaction mix in the Reactor Cyclones and stored at 510°C (950°F) in the Char Surge Hopper. The 510°C (950°F) char flows to the Char Heater where a portion of the char is burned to raise the temperature of the circulating char to 760°C (1400°F). Combustion gases are separated from the char in the Char Heater Cyclones and the heated char is stored at 760°C (1400°F) in the Heated Char Seal Hopper. The 760°C (1400°F) char flows from the hopper to join the shredded bark from the Reactor Screw Feeder ahead of the Reactor. The net char make is withdrawn at 510°C (950°F) from the Char Surge Hopper and quenched with water to 121°C (250°F) in the Char Make Hopper. The Hot Char Conveyor transports the product char to char storage.

The 510°C (950°F) reaction mix from the Reactor Cyclones (containing the net bark oil, wax, and pyrolysis gas products) is contacted with circulating quench oil in the Quench Venturi and cooled to 80°C (175°F). At these conditions the bark oil and wax is condensed and separated from the remaining pyrolysis gases in the Decanter. The Decanter also provides 30 minutes residence time for the quench oil which is sufficient to give good separation of the bark oil from the circulating quench oil. The net bark oil product is withdrawn from the decanter and pumped to product storage. Off spec and Rundown Tanks are also provided if further processing is required before the bark oil is pumped to storage. A slip stream of the circulating quench is fed to Wax Removal Facilities where the net wax make is removed from the system.

A small portion of the condensed bark oil is entrained as a fine mist with the pyrolysis gases from the Decanter. This entrained bark oil is scrubbed from the gas stream by washing the stream with quench oil through the Demister Venturi. The quench and bark oil are separated from the gas in the Demister Pot and returned to the Decanter to separate the bark oil from the quench. The gas from the Demister Pot is compressed to 1 atmg (15 psig) and recycled to the pyrolysis area as transport and fuel gas.

PLOT PLAN

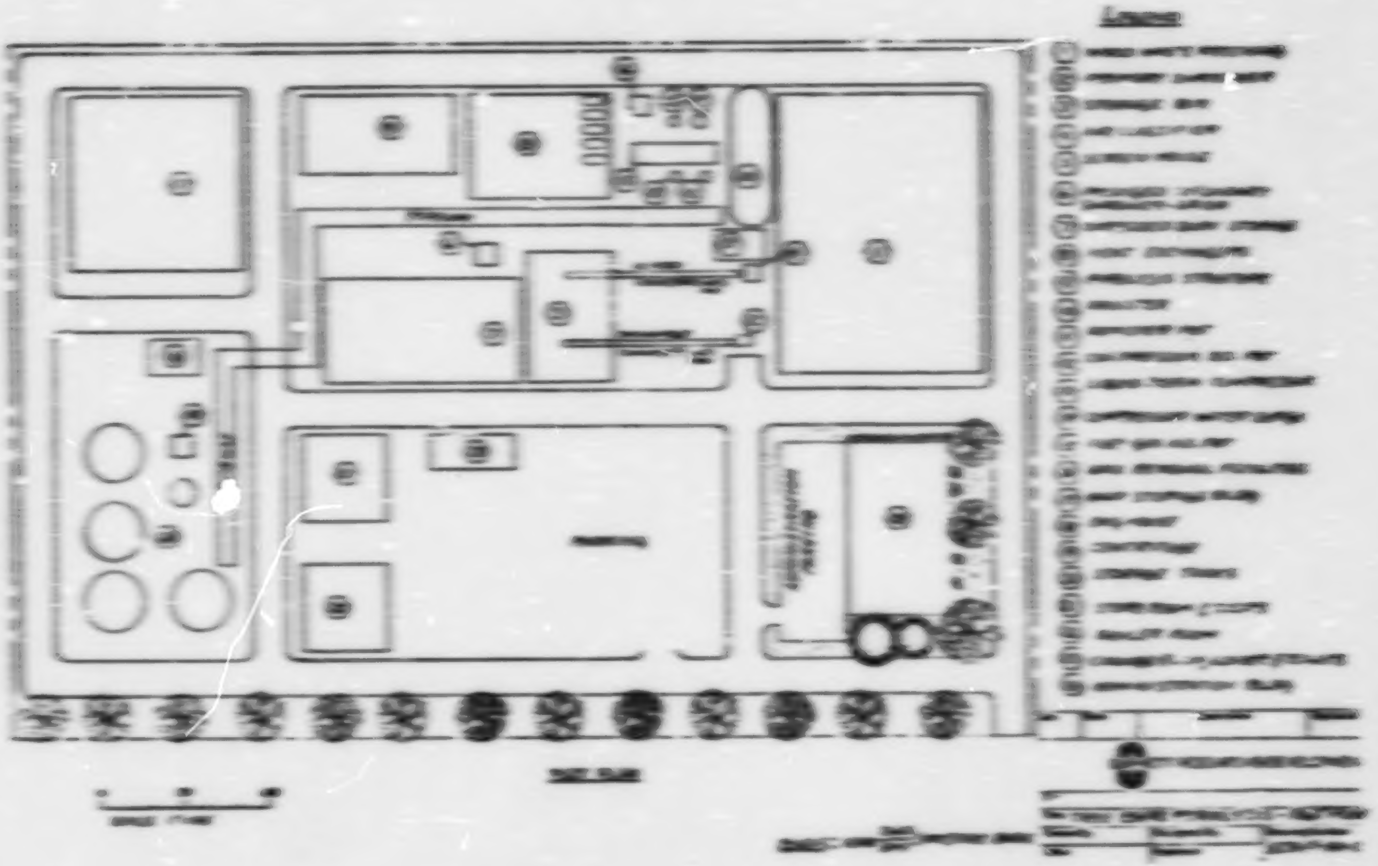
A typical plot layout for a 1200 Ton per day Tree Bark Pyrolysis plant is shown on Figure IV-2. Total area requirement for a plant this size is about 22,000-24,000 m^2 (5-1/2 to 6 acres) including all storage, shops, offices, parking, etc. A plot layout for a 300 Ton per day plant is not shown, but, using a similar arrangement, the area requirement would be about 16,000 m^2 (4 acres).

EQUIPMENT DISCUSSION

Figure IV-1 presents the Process Flow Diagram and a material balance for a feed rate of 1200 Tons per day (dry) to the primary shredder. Tables IV-9 and IV-10 present a detailed list of the equipment required. Sufficient receiving and intermediate storage is provided to permit the processing plant to operate at design rates, 24 hours per day, 350 days per year.

Primary Shredder

The Primary Shredder reduces the size of the raw bark to 80% less than 8 cm (3 inch) particles. This is a necessary first step to permit effective separation of rocks, earth, and other inorganics from the raw bark and to provide an optimum feed to the Secondary Shredder-Drier unit.



Criteria for primary shredding equipment at a commercial plant include:

1. Mill capacity, when producing a 8 cm (3 inch) product, should be great enough so that only two units, one operating and one spare, are needed.

2. On-size material should be removed from the mill as quickly as possible to minimize the production of inorganic fines which are difficult to separate from the shredded bark.

3. No pretreatment or preselection of the feed should be required.

Air Classifier

The Air Classifier serves to separate the oversize bark greater than 8 cm (3 inch) for recycle to the Primary Shredder and to also separate the denser inorganic substances from the lighter 8 cm (3 inch) and less bark which is to be further shredded, dried and pyrolysed. The rough separation is made according to density, size, and aerodynamic characteristics of the shredded mixture.

A classifier may be built as a zig-zag, straight vertical, straight horizontal, or other suitable unit. Studies have shown that the zig-zag principle is the most efficient in that it allows the separation of materials with closely similar densities and with other properties (e.g. size) that are almost identical. A typical unit consists of a vertical zig-zag column with multiple stages and upward air circulation. The feed is introduced part way up the column. Lighter components are carried out the top of the unit with the air stream, and are then removed by an external cyclone. Heavy inorganic substances such as glass, metals, stones, etc., which cannot be transported up through the column at the chosen air velocity, fall out at the bottom of the unit along with the heavier oversize chunks of bark. Simple screening of the underflow from the air classifier removes the inorganics from the larger bark fraction.

It is important that the inorganic fraction in the stream elutriated from the top of the classifier be as small as possible. Otherwise, the hard, abrasive inerts will cause substantial wear in downstream equipment such as the secondary grinding mills, transfer lines, and cyclones. The inorganics also increase the ash content of the pyrolytic oil and char, and may result in a loss of revenue, owing to off-specification products.

Secondary Shredder-Drier

The Secondary Shredder-Drier unit proposed is an apparatus in which the 8 cm (3 inch) and smaller bark from the air classifier overhead is simultaneously shredded to 80% less than 24 mesh particles and dried to 5 wt % moisture. High yields of oil from the pyrolysis of organic solids are obtained by the extremely rapid transfer of heat to small particles, which requires that the feed be shredded to a nominal minus 24 mesh.

Raw bark is fed to the grinding chamber along with hot, inert gas. In the grinding chamber, rotating hammers reduce the particle size to minus 24 mesh while the hot gas simultaneously removes moisture. Drying in the system is greatly accelerated by the increased surface area as the particle size is reduced.

The flow of hot gas selectively air-conveys particles smaller than 24 mesh up and out of the grinding chamber. The air suspended, ground product passes through an adjustable velocity separator where a size classification is made. This separator returns any oversize material to the grinding chamber while product sized material is air conveyed away. The minus 24 mesh bark is separated from the air stream in a cyclone separator and the fines from the cyclone are removed from the air stream by a fabric dust collector. A small amount of the fines may need to be burned as fuel in the drier to supplement the pyrolysis gases. The integrated Secondary Shredder-Drier system is commercially proven and readily available.

Pyrolysis

The pyrolysis process is based on the rapid heating of organic materials, using a proprietary heat-exchange system. Dry, finely shredded waste is delivered by a screw feeder into the transport line, where it is picked up by recycled gas and carried to the pyrolysis reactor. Rapid and complete pyrolysis takes place at an elevated temperature (510°C, 950°F) as the feed travels upwards under turbulent flow conditions. The only pressure required is that which must be provided to move material through the system. The maximum system pressure is generally less than 1 atmg (15 psig). The technology involved in the char hoppers and circulation system is well known through such application as oil refinery fluid catalytic cracking (FCC) units, etc.

Char particle size and cyclone design are closely related and critical to the successful operation of the circulating char heat exchange system. This aspect of the design and operation must be carefully considered and closely controlled.

Residence time in the reactor is relatively short - a few seconds or less - to obtain the product yield structure indicated. The reaction mix must be removed from the reaction zone quickly before cracking into carbon, lighter fractions, and gas can occur. The quenching step that follows must therefore be closely coupled to the reactor.

Liquid Collection and Storage

The gases leaving the reactor contain char, pyrolysis gases, condensible vapors, and recycle transport gas. After the char is removed by the hot cyclones in the reactor unit, the reaction mix is quickly quenched in a venturi quench system to about 80°C (175°F) to recover the pyrolysis oil before thermal cracking can take place. The Quench Venturi is a highly efficient contacting device which operates on the principle of heat exchange by direct contact of the hot reaction mix with finely dispersed droplets of cold quench. The technology involved is well known and commercial units are readily available. Pressure drop is low (13-15 cm of water (5-6 inches WG)) but heat transfer is quite rapid.

The quenched reaction mix and quench fluid flow to the Decanter vessel. This vessel is designed for high liquid residence time and good separation between outlet vapor and liquid streams. The bark oil is effectively separated from the circulating quench fluid by gravity settling, but experience indicates that a significant amount of finely dispersed bark oil remains entrained in the outlet vapor stream. This vapor stream is therefore further cooled and scrubbed using the Demister Venturi.

The Demister Venturi operates with a relatively high pressure drop (75-100 cm of water (30-40 inches WG)) and effectively scrubs the entrained oil droplets from the vapor stream. Efficiencies are in the order of 98-99% droplet recovery. Close control of the temperature in the Demister indirectly provides control of the water content of the product bark oil by controlling the amount of water condensed from the vapor stream.

Vapor from the Demister is compressed to 1 atmg (15 psig), using a liquid seal compressor such as a Nash Pump. This type of unit is specified to provide reliability and to minimize down time and maintenance time required by the presence of corrosive and abrasive materials, e.g. residual fine particles of char in the gas stream.

ECONOMIC EVALUATION

The bases for the design and the equipment requirements for the plant are described above. For the 1200-ton-per-day plant, Tables IV-2 and IV-3 summarize the capital costs and Table IV-4 presents a detailed breakdown of the capital cost estimate. The operating cost estimate is shown in Table IV-6 and is summarized on Table IV-5. A manpower summary is presented in Table IV-8 and Figure IV-3 shows the proposed project schedule.

Similarly, for the 300-ton-per-day plant, the capital costs breakdown and summaries are presented in Tables IV-10, IV-8 and IV-9, respectively. Table IV-12 shows the detailed operating cost estimate and the operating cost summary is presented on Table IV-11. All costs are based on February, 1974 data.

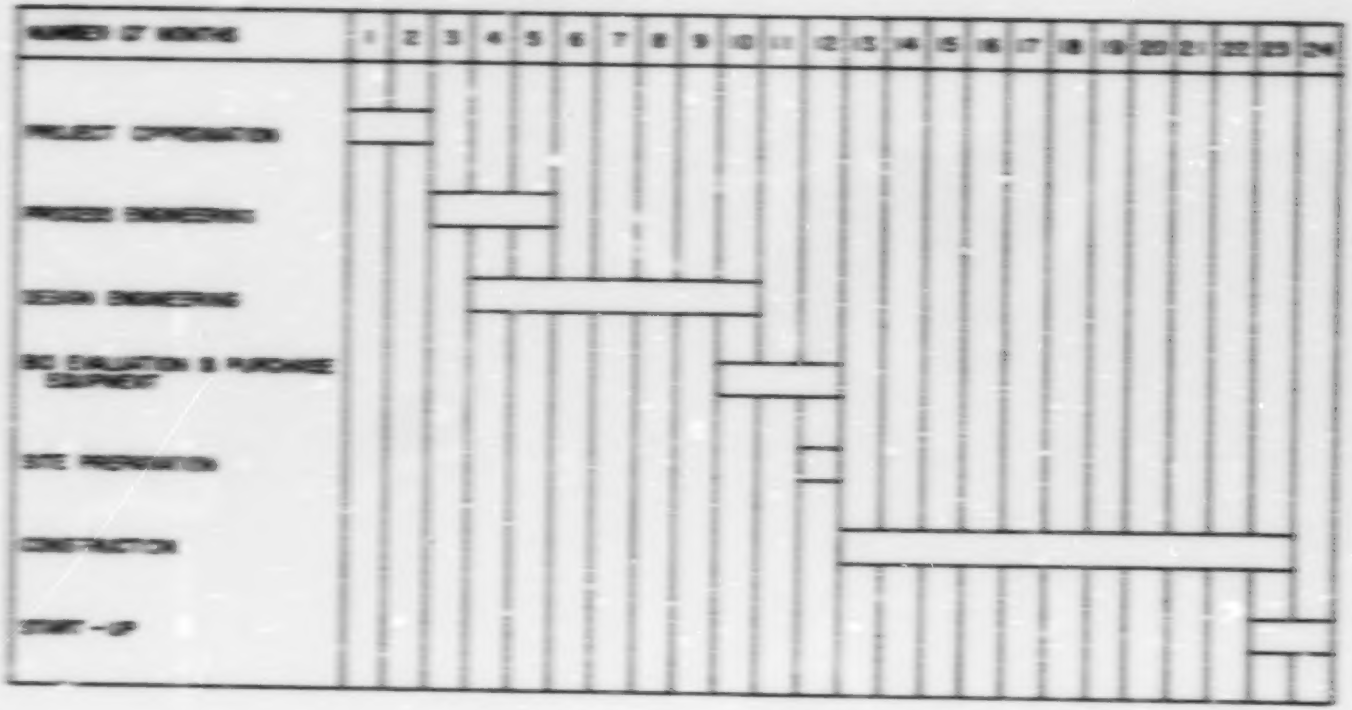
Estimated product revenues are:

Product	Value ($/ton)	Revenue ($/ton of dry bark)		
Bark Oil	42	15.50	15.50	15.50
Char - Fuel	5	1.15	-	-
- Charcoal Briquettes	20	-	4.60	-
- Activated Carbon	40	-	-	9.20
TOTALS		$16.25	$20.10	$24.70

The yield of oil obtained is approximately 0.28 m^3/dry ton (1.75 bbl/ton) with a heating value averaging 5.8 Kcal/g (10,500 Btu/lb). The oil is a low-sulfur fuel with some of the characteristics of No. 6 heating oil, the standard fuel for utility plants.

The economics presented below for the 300-ton-per-day and the 1200-ton-per-day commercial pyrolysis plants are based on the data obtained from the continuous pilot plant processing tan bark as discussed in Phase II of this report. As shown below, the 300-ton-per-day plant will essentially break even when selling heating oil and charcoal briquettes, but the 1200-ton-per-day plant produces a fair return on investment on the basis of bark oil sales alone.

FIGURE III-3
PROJECT SCHEDULE
TREE BARK PYROLYSIS FACILITY



	Nominal Feed Rate (dry basis)	
Item	300 Ton/Day	1200 Ton/Day
Capital Cost (Excluding land)	$4,960,000	$13,310,000
Annual Operating Cost	1,717,000	2,857,000
Cost per Ton (including Plant Amortization)	21.18	10.03
Revenue from Sale of Oil and Char:		
Barkoil Only	15.50	15.50
plus Char as Fuel	16.65	16.65
Char as Briquettes	20.10	20.10
Char as Activated Carbon	24.70	24.70

At a 300 ton/day scale, the operating cost is projected at $21.18 and revenues of $16.65 to 24.70 per dry ton of bark, depending upon the value of the char produced. At a 1200 ton/day scale, revenues remain the same, but projected operating costs (including plant amortization but excluding land costs) drop to $10.03 per Ton.

ENVIRONMENTAL CONSIDERATIONS

The pyrolysis process will greatly reduce the difficulties of meeting not only the pollution control regulations of today, but the stricter standards of the future. An environmental balance for the 300 Ton per day plant is shown in Figure IV-3 and a balance for the 1200 Ton per day plant is shown in Figure IV-4. It can be seen that the quantity of sterile solids going to landfill consists only of rocks and dirt carried in with the bark. Much thought has been given to minimizing air pollution. Because it is a totally contained operation from which air is excluded, the Flash Pyrolysis process has intrinsic advantages in this respect and the gaseous emissions will be significantly reduced. Air pollution problems are also minimized by the care taken in handling air or gas streams from the classifier and secondary shredder-drier.

FIGURE IV-4
SYSTEM ENVIRONMENTAL BALANCE
TREE BARK PYROLYSIS
1200 T/D (DRY)

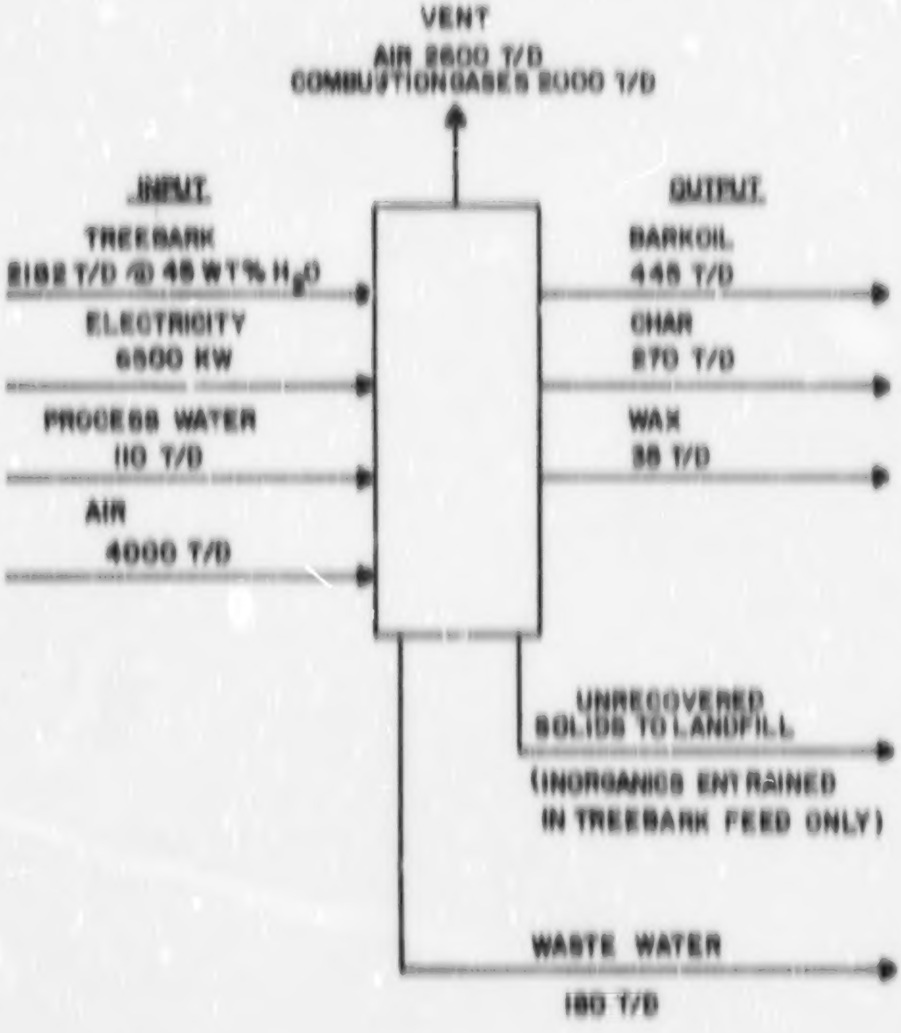
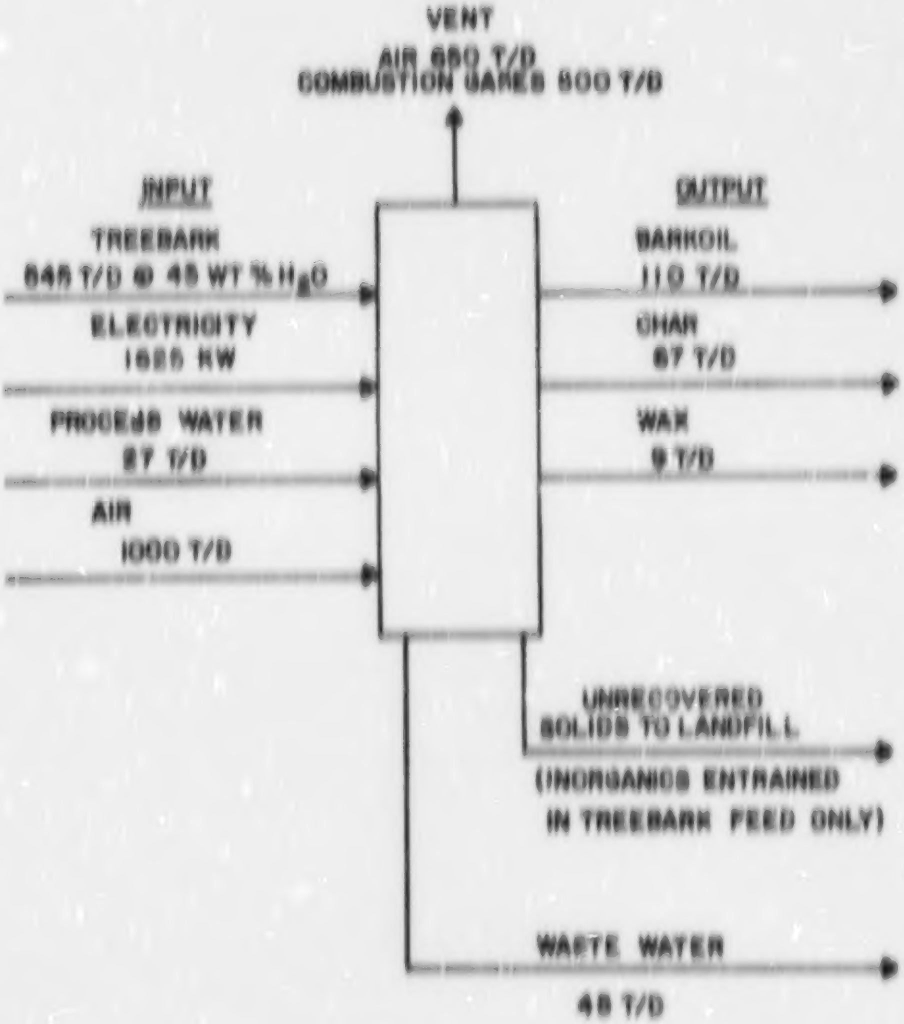

VENT
AIR 2600 T/D
COMBUSTIONGASES 2000 T/D
INPUT
TREEBARK
2182 T/D @ 45 WT% H_2O
ELECTRICITY
6500 KW
PROCESS WATER
110 T/D
AIR
4000 T/D
OUTPUT
BARKOIL
445 T/D
CHAR
270 T/D
WAX
35 T/D
UNRECOVERED
SOLIDS TO LANDFILL
(INORGANICS ENTRAINED
IN TREEBARK FEED ONLY)
WASTE WATER
180 T/D

FIGURE IV-5

SYSTEM ENVIRONMENTAL BALANCE

TREE BARK PYROLYSIS

500 T/D (DRY)


VENT
AIR 650 T/D
COMBUSTION GASES 500 T/D
INPUT
TREEBARK
845 T/D @ 45 WT % H_2O
ELECTRICITY
1625 KW
PROCESS WATER
27 T/D
AIR
1000 T/D
OUTPUT
BARKOIL
110 T/D
CHAR
67 T/D
WAX
9 T/D
UNRECOVERED
SOLIDS TO LANDFILL
(INORGANICS ENTRAINED
IN TREEBARK FEED ONLY)
WASTE WATER
48 T/D

The secondary shredder-drier is blanketed by an inert gas stream operating on total recycle in order to eliminate any fire hazard. All conveying gases are thus eventually passed through the process heater where odors are destroyed and carbonaceous particles are burned at a temperature of 982°C (1800°F). This single gaseous effluent from the entire process is then cooled to 121°C (250°F) and filtered to remove any traces of ash and inert contaminants. The gases vented to atmosphere consist primarily of air and products of combustion containing traces of SO_x and NO_x. The projected environmental impact as a result of this project is expected to be as follows:

Noise

The process utilizes a variety of machinery to transport, shred, classify and pulverize the as-received material. All of this equipment will be installed in such a manner that the sound intensities at the plant boundary are expected to be less than 55 decibels (dB).

Stack Gas Emissions

The total quantity of gaseous emmissions from the proposed 1200 Ton per day plant is expected to be 2000 Tons per day. This entire stream is filtered and discharged through a single stack. The stack gases will have the following characteristics based upon 12.5 volume percent CO_2:

SO_x	0.02 vol %
NO_x	60 ppm
Particulates	0.07 g/m^3 (0.03 gr/scf)

Liquid Effluents

The quantity of water produced by pyrolysis at the 1200 Ton per day unit and discharged from the system as liquid is 180 Tons per day. This water contains only small quantities of dissolved solids, but could have a COD content as high as 100,000 ppm. However, there are no water disposal problems, provided secondary sewage treatment facilities are available.

Table IV-2. CAPITAL COST ESTIMATE - 2200 T/D

Plant	Equipment Cost,$	Installation Factor	Installed Cost,$
Primary Shredding	781,000	1.8	1,420,000
Secondary Shredding	1,160,000	2.0	2,320,000
Pyrolysis	490,000	3.0	1,800,000
Liquid Collection & Storage	1,021,000	2.5	2,550,000
Offsite	-	-	1,810,000
Total Equipment Cost	3,565,000	Installed Cost	9,900,000
		A/E (7 1/2%)	744,000
		GSA Cost (4 1/2%)	447,000
		TOTAL	11,091,000
		Contingency (20%)	2,219,000
		Total Cost Estimate	13,310,000

Table IV-3. CAPITAL COSTS BY AREA - 1200 T/D

Primary Shredding		
Installed Cost	$1,420,000	
GR&D + A/E (12%)	171,000	
	$1,591,000	
Contingency (20%)	318,000	
	$1,909,000	$ 1,909,000
Secondary Shredding		
Installed Cost	2,320,000	
GR&D + A/E (12%)	279,000	
	$2,599,000	
Contingency (20%)	520,000	
	$3,119,000	$ 3,119,000
Pyrolysis		
Installed Cost	1,800,000	
GR&D + A/E (12%)	216,000	
	$2,016,000	
Contingency (20%)	403,000	
	$2,419,000	$ 2,419,000
Liquid Collection		
Installed Cost	2,550,000	
GR&D + A/E (12%)	307,000	
	$2,857,000	
Contingency (20%)	572,000	
	$3,429,000	$ 3,429,000
Offsites		
Installed Cost	1,810,000	
GR&D + A/E (12%)	218,000	
	$2,028,000	
Contingency (20%)	406,000	
	$2,434,000	$ 2,434,000
		$13,310,000

Table IV-4. EQUIPMENT LIST - 1200 T/D

Item	Service	Estimated Cost
	PRIMARY SHREDDING	
Materials Handling		
	Raw Bark Conveyor	$ 35,000
	Pan Feed Conveyor	30,000
	Primary Shredder	160,000
	Discharge Conveyor	35,000
	Air Classifier Recycle Conveyor	25,000
	Rotary Valve	2,000
	Distribution Conveyor	10,000
	Shredded Bark Conveyor	25,000
	Air Classifier Feed Conveyor	73,000
Blowers/Fans		
	Air Classifier Circulation & Vent Fans	35,000
Separation Equipment		
	Air Classifier	80,000
	Air Classifier Cyclone	2,000
	Screen	25,000
Tanks/Bins		
	Landfill Bin	1,000
	Shredded Storage Bin	250,000
	(TOTAL)	$788,000
	SECONDARY SHREDDING	
Materials Handling		
	Secondary Shredder-Drier	1,030,000
	Reactor Screw Feeder	50,000
	Delumper	20,000
Tanks/Bins		
	Reactor Surge Storage	60,000
	(TOTAL)	$1,160,000

Table IV-4. EQUIPMENT LIST - 1000 T/D (cont.)

PYROLYSIS SECTION

Item	Service	Estimated Cost,$
Materials Handling		
	Hot Char Conveyor	10,000
Reactors		
	Reactor	15,000
	Char Heater	15,000
Separation Equipment		
	Reactor Cyclones	35,000
	Char Heated Cyclones	35,000
Tanks/Bins		
	Reactor Char Surge Hopper	70,000
	Char Heater Surge Hopper	30,000
	Char Make Hopper	25,000
Miscellaneous		
	Slide Valves	80,000
	Flapper Valves	15,000
	Pyrolysis Structure	170,000
	TOTAL	600,000

Table IV-4. EQUIPMENT LIST - 1200 T/D (cont.)

LIQUID COLLECTION AND STORAGE

Item	Service	Estimated Cost,$
Heat Exchangers		
	Quench Cooler	150,000
	Demister Cooler, Sealwater Cooler & Recycle Cooler	30,000
Compressors		
	Fuel Gas Compressor	350,000
Pumps		
	Rundown Tank Pump	2,300
	Decanter Product Pump & Spare	7,000
	Decanter Quench Pump & Spare	17,800
	Demister Venturi Pump	4,600
	Decanter Feed Pump	3,000
	Product Oil Pump & Spare	7,000
	Seal Water Pump	4,000
Separation Equipment		
	Rundown Centrifuge	75,000
	Line Filters	6,000
Tanks/Bins		
	Rundown Tanks	40,000
	Off - Spec. Tank	24,000
	Product Tanks	50,000
	Quench Oil Storage	35,000
Vessels		
	Demister Pot	14,000
	Compressor KO Pot	14,000
	Fuel Gas KO Pot	14,000
	Decanter	60,000
	Compressor Water Surge Pot	4,000
Miscellaneous		
	Quench Venturi	42,000
	Demister Venturi	30,000
	TOTAL	1,021,000

Table IV-4. EQUIPMENT LIST - 1200 T/D (cont.)

OFFSITE

Item	Service	Estimated Cost,$
Equipment		
	Flare	
	Bag Filter House	
	Steam Generator	
	Liquid Nitrogen Storage	
	Power Substation	
	Instrument Air Compressor	
	Char Storage	
	Laboratory Equipment	
	Tools	
	Spare Parts	
	Plant Vehicles	
Installed Cost @ 15 % of	Onsite Plant Installed Cost	1,210,000
Buildings		
	Operations/ Maintenance/Lab	400,000
	Administration	200,000
	TOTAL	1,810,000

Table IV-5. SUMMARY OF OPERATING COSTS - 1200 T/D

Costs by Area	$/Year	$/Ton Dry Feed
Primary Shredding	655,000	1.56
Secondary Shredding	537,000	1.27
Pyrolysis	443,000	1.05
Liquid Collection & Storage	773,000	1.85
Offsites & Miscellaneous	451,000	1.07
TOTAL	2,857,000	6.80
Costs by Category		
Labor (63 total)	660,000	1.57
Supervision	165,000	0.39
Maintenance	705,000	1.68
Utilities	512,000	1.22
Taxes & Insurance	399,000	0.95
Overhead G & A	349,000	0.83
Other Costs	67,000	0.16
TOTAL	2,857,000	6.80
Capital Charge (20 years @ 8 %)	1,358,000	3.23
	4,215,000	10.03*

* $10.03/Ton (DRY) is equivalent to $5.51/Ton "As Received" wet tree bark.

Table IV-6. OPERATING COSTS ESTIMATE - 1200 T/D

1200 T/d for 350 operating days/year = 420,000 T/year

Capital Cost Estimate = $ 13,310,000

Labor Estimate

Operating	33	(All Shifts)
Maintenance	18	(Day Shift)
Supervision	9	(All Shifts)
Admin. & Other	14	(Day Shift)
		74 TOTAL

Primary Shredding

Capital Cost Estimate $ 1,905,000

Operating Costs

Variable	**$/Year**	**$/Ton Dry Feed**
Electric power 1300 KW × 16 $\frac{hr.}{day}$ × 350 × $\frac{1¢}{KWH}$	73,630	0.18
Fixed		
Labor 4 shift × $60,000	240,000	0.57
Supervision (25% of op. labor)	60,000	0.14
Maintenance		
Labor (1.3% of capital)	25,000	0.06
Mat'l (4.0% of capital)	76,000	0.18
Operating Supplies (0.5% of capital)	10,000	0.02
Overhead G&A (35% of labor total)	114,000	0.28
Taxes & Insurance (3% of capital)	57,000	0.14
TOTAL FIXED	582,000	1.38
TOTAL OPERATING COSTS	655,000	1.56

Table IV-6. OPERATING COST ESTIMATE - 1200 T/D (cont.)

Secondary Shredding

Capital Cost Estimate $3,119,000

Operating Costs

Variable	$/Year	$/Ton Dry Feed
Electric power 1700 KW x 24 hrs x 350 days x $\frac{1¢}{KWH}$	143,000	0.34
Fixed		
Labor 1 shift x $60,000	60,000	0.14
Supervision (25% of op. labor)	15,000	0.04
Maintenance		
Labor (1.3% of capital)	41,000	0.10
Mat'l (4.0% of capital)	125,000	0.30
Operating Supplies (0.5% of capital)	16,000	0.04
Overhead G&A (35% of total labor)	41,000	0.10
Taxes & Insurance (3% of capital)	94,000	0.22
TOTAL FIXED	392,000	0.93
TOTAL OPERATING COSTS	$535,000	1.27

Table IV-6. OPERATING COST ESTIMATE - 1200 T/D (cont.)

Pyrolysis

Capital Cost Estimate $2,419,000

Operating Costs

Variable	$/Year	$/Ton Dry Feed
Electric power 200 KW x 24 hrs x 350 days x 1¢/KWH	17,000	0.04
Water 8GPM @ 30¢/1000 gal.	1,000	--
TOTAL VARIABLE	18,000	0.04
Fixed		
Labor 2 shift x $60,000	120,000	0.29
Supervision (25% of op. labor)	30,000	0.07
Maintenance Labor (1.3% of capital)	31,000	0.07
Mat'l (4.0% of capital)	97,000	0.23
Operating Supplies (0.5% of capital)	12,000	0.03
Overhead G&A (35% of total labor)	63,000	0.15
Taxes & Insurance (3% of capital)	72,000	0.17
TOTAL FIXED	425,000	1.01
TOTAL OPERATING COSTS	443,000	1.05

Table IV-6. OPERATING COST ESTIMATE - 1200 T/D (cont.)

Liquid Collection & Storage

Capital Cost Estimate $ 3,429,000

Operating Costs

Variable	**$/Year**	**$/Ton Dry Feed**
Electric Power 3000 KW × 24 × $\frac{1¢}{KWH}$	252,000	0.60
Water 10 GPM @ $\frac{20¢}{1000\ gal.}$	1,000	-
Total Variable	253,000	0.60
Fixed		
Labor 2/shift × 60,000	120,000	0.28
Supervision	30,000	0.07
Maintenance		
Labor (1.3 % of Capital)	45,000	0.11
Material (4 % of Capital)	137,000	0.33
Operating Supplies (0.5 % of Capital)	17,000	0.05
Overhead G & A (3.5 % of Total Labor)	68,000	0.16
Taxes & Insurance (3 % of Capital)	103,000	0.25
Total Fixed	520,000	1.25
Total of Costs	773,000	1.85

Table IV-6. OPERATING COST ESTIMATE - 1200 T/D (cont.)

Offsites & Miscellaneous

Capital Cost Estimate $ 2,434,000

Operating Costs

Variable	**$/Year**	**$/Ton Dry Feed**
Electric Power 300 KW x 24 x 350 x 1¢/KWH	25,000	0.06
Fixed		
Labor 3/shift x 40,000	120,000	0.29
Supervision	30,000	0.07
Maintenance Labor (1.3 % Of Capital)	31,000	0.07
Maintenance Material (4 % of Capital)	97,400	0.23
Operating Supplies (0.5 % of Capital)	12,000	0.03
Overhead G & A (35 % of Total Labor)	63,000	0.15
Taxes & Insurance (3 % of Capital)	73,000	0.17
Total Fixed	426,000	1.01
Total of Costs	451,000	1.07

Table IV-7 MANPOWER SUMMARY - 300 & 1200 T/D PLANTS

Primary Shredding	
2	Shredder Operations
1	Storage & Bin Handling
1	Conveyors & Air Classifier
Secondary Shredding	
1	Shredder Operator
Pyrolysis	
1	Reactor Control Room
1	Char Heater, Char Handling
Liquid Collection & Storage	
1	Compressor House
1	Quench / Collection
Offsites	
1	Storage - Product Shipping
1	Utilities
Supervision	
1	Recieving & Feed Preparation
1	Utilities, Offsites, Maintenance
Engineering	
1	Mechanical Engineer (1 shift Only)

Table IV-7. MANPOWER SUMMARY - 300 & 1200 T/D PLANTS (cont.)

Maintenance

1200 T/D Plant

5.3 % of Capital = (.053)($ 13,310,000)
= $ 705,000
Labor = 1.3 % 173,000 (11 men)
Materials = 4.0 % 532,000
$ 705,000

300 T/D Plant

5.3 % of Capital = (.053)($ 4,960,000)
= $ 263,000
Labor = 1.3 % 65,000 (4 men)
Materials = 4.0 % = 198,000
$ 263,000

Table IV-9. CAPITAL COSTS BY AREA - 300T/D

Primary Shredding		
Installed Cost	$640,000	
GR&D + A/E (12 %)	77,000	
	717,000	
Contingency (20 %)	143,000	
	860,000	$ 860,000
Secondary Shredding		
Installed Cost	$760,000	
GR&D + A/E (12 %)	91,000	
	851,000	
Contingency (20 %)	170,000	
	1,021,000	$1,021,000
Pyrolysis		
Installed Cost	$600,000	
GR&D + A/E (12 %)	72,000	
	672,000	
Contingency (20 %)	135,000	
	807,000	$ 807,000
Liquid Collection		
Installed Cost	$950,000	
GR&D + A/E (12 %)	114,000	
	1,064,000	
Contingency (20 %)	213,000	
	1,277,000	$1,277,000
Offsite		
Installed Cost	$740,000	
GR&D + A/E (12 %)	89,000	
	829,000	
Contingency (20 %)	166,000	
	995,000	$ 995,000
		$4,960,000

Table IV-10. EQUIPMENT LIST - 100 T/D

Item	Service	Estimated Cost
	PYROLYSIS SECTION	
Materials Handling		
	Hot Char Conveyor	$ 5,000
Separation Equipment		
	Reactor Cyclones	25,000
	Char Heater Cyclones	20,000
Tanks/Bins		
	Reactor Char Surge Hopper	30,000
	Char Heater Surge Hopper	20,000
	Char Make Hopper	15,000
Miscellaneous		
	Slide Valves	25,000
	Flapper Valves	5,000
	(TOTAL)	$145,000
	PRIMARY SHREDDING	
Materials Handling		
	Raw Bark Conveyor	$ 23,000
	Pan Feed Conveyor	20,000
	Primary Shredder	75,000
	Discharge Conveyor	15,000
	Air Classifier Recycle Conveyor	11,000
	Rotary Valve	2,000
	Distribution Conveyor	8,000
	Shredded Bark Conveyor	15,000
	Air Classifier Feed Conveyor	25,000
Blowers/Fans		
	Air Classifier Circulation & Vent Fans	13,000
Separation Equipment		
	Air Classifier	37,000
	Air Classifier Cyclone	2,000
	Screen	13,000
Tanks/Bins		
	Landfill Bin	1,000
	Shredded Storage Bin	100,000
	(TOTAL)	$355,000

Table IV-16. EQUIPMENT LIST - 300 T/D (cont.)

Item	Service	Estimated Cost
	SECONDARY SHREDDING	
Materials Handling		
	Secondary Shredder - Drier	$300,000
	Reactor Screw Feeder	40,000
	Delumper	15,000
Tanks/Bins		
	Reactor Surge Storage	25,000
	(TOTAL)	$380,000
	LIQUID COLLECTION & STORAGE	
Heat Exchangers		
	Quench Cooler	$ 70,000
	Demister Cooler, Sealwater Cooler & Recycle Cooler	8,000
Compressors		
	Fuel Gas Compressor	100,000
Pumps		
	Rundown Tank Pump	800
	Decanter Product Pump & Spare	1,600
	Decanter Quench Pump & Spare	5,400
	Demister Venturi Pump	1,200
	Decanter Feed Pump	900
	Product Oil Pump & Spare	1,100
	Seal Water Pump	1,000
Separation Equipment		
	Rundown Centrifuge	30,000
Tanks/Bins		
	Rundown Tanks	10,000
	Off-Spec. Tank	8,000
	Product Tanks	80,000
	Quench Oil Storage	15,000
Vessels		
	Demister Pot	6,000
	Compressor KO Pot	7,000
	Fuel Gas KO Pot	5,000
	Decanter	60,000
	Compressor Water Surge Pot	3,000

Table IV-10. EQUIPMENT LIST - 300 T/D (cont.)

Item	Service	Estimated Cost
	LIQUID COLLECTION & STORAGE	
Miscellaneous		
	Quench Venturi	$ 15,000
	Demister Venturi	11,000
	(TOTAL)	$380,000
	OFFSITE	
Equipment		
	Flare	
	Bag Filter House	
	Steam Generator	
	Liquid Nitrogen Storage	
	Power Substation	
	Instrument Air Compressor	
	Char Storage	
	Laboratory Equipment	
	Tools	
	Spare Parts	
	Plant Vehicles	
Installed Cost @ 15 % of Onsite	Plant Installed Cost	$440,000
Building		
	Operations/Maintenance/Lab	200,000
	Administration	100,000
	(TOTAL)	$740,000

Table IV-11. SUMMARY OF OPERATING COSTS - 300 T/D

	$/Year	$/Ton Dry Feed
Costs By Area		
Primary Shredding	502,000	4.78
Secondary Shredding	232,000	2.21
Pyrolysis	280,000	2.67
Liquid Collection & Storage	383,000	3.65
Offsites & Miscellaneous	320,000	3.05
TOTAL	1,717,000	16.36
Costs By Category		
Labor (63 total)	660,000	6.29
Supervision	165,000	1.57
Maintenance	262,000	2.50
Utilities	146,000	1.39
Taxes & Insurance	149,000	1.42
Overhead G&A	311,000	2.96
Other Costs	24,000	0.23
TOTAL	1,717,000	16.36
Capital Charge (20 years @ 8 %)	506,000	4.82
TOTAL COSTS	2,223,000	21.18

*$21.18/Ton (DRY) is equivalent to $11.65/Ton "As Received" Wet tree bark

Table IV-12. OPERATING COST ESTIMATE - 300 T/D

300 T/D for 350 Operating Days Per Year = 105,000 T/Year

Capital Cost Estimate $ 4,960,000

Labor Estimate

Operating	11	(All Shifts)
Maintenance	4	(Day Shift)
Supervision	2	(All Shifts)
Administrative & Other	11	(Day Shift)
	67	Total

Primary Shredding

Capital Cost Estimate $ 860,000

Operating Costs

Variable	$/Year	$/Ton Dry Feed
Electric Power		
325 KW x 16 hr/day x 350 x 1¢/KWH	18,000	0.17
Fixed		
Labor 4/Shift x $ 60,000	240,000	2.29
Supervision 25 % of Operating Labor	60,000	0.57
Maintenance Labor (1.3 % of Capital)	11,000	0.10
Maintenance Materials (4 % of Capital)	34,000	0.32
Operating Supplies (0.5 % of Capital)	4,000	0.04
Overhead G&A (35 % of Labor Total)	109,000	1.04
Taxes & Insurance (3 % of Capital)	26,000	0.25
Total Fixed	484,000	4.61
Total Operating Costs	502,000	4.78

Table IV-12. OPERATING COST ESTIMATE - 300 T/D (cont.)

Secondary Shredding

Capital Cost Estimate $ 1,032,000

Operating Costs

	$/Year	$/Ton Dry Feed
Variable		
Electric Power		
425 KW x 24 hours x 353 days x 1¢/KWH	36,000	0.34
Fixed		
Labor 1/Shift x 60,000	60,000	0.57
Supervision (25 % of Operating Labor)	15,000	0.14
Maintenance Labor (1.3 % of Capital)	13,000	0.12
Maintenance Material (4 % of Capital)	41,000	0.39
Operating Supplies (0.5 % of Capital)	5,000	0.05
Overhead G & A (35 % of Labor)	31,000	0.30
Taxes & Insurance (3 % of Capital)	31,000	0.30
Total Fixed	196,000	1.87
Total Operating Costs	232,000	2.21

Table IV-13. OPERATING COST ESTIMATE - 300 T/D (cont.)

Pyrolysis

Capital Cost Estimate $ 806,000

Operating Costs

	$/Year	$/Ton Dry Feed
Variable		
Electric Power		
50 KW x 24 hours x 350 days x 1¢/KWH	4,000	0.04
Water		
2 GPM @ 30¢/100 gal.	-	0
Total Variable	4,000	0.04
Fixed		
Labor 2/Shift x 60,000	120,000	1.14
Supervision (25 % of Operating Labor)	30,000	0.29
Maintenance Labor (1.3 % of Capital)	10,000	0.10
Maintenance Materials (4 % of Capital)	32,000	0.30
Operating Supplies (0.5 % of Capital)	4,000	0.04
Overhead G & A (35 % of Total Labor)	56,000	0.53
Taxes & Insurance (3 % of Capital)	24,000	0.23
Total Fixed	276,000	2.63
Total Operating Costs	280,000	2.67

Table IV-12. OPERATING COST ESTIMATE - 300 T/D (cont.)

Liquid Collection & Storage

Capital Cost Estimate $ 1,277,000

Operating Costs

	$/Year	$/Ton Dry Feed
Variable		
Electric Power		
750 KW x 24 x 350 x 1¢/KWH	63,000	0.60
Water		
3 GPM @ 20¢/1000 gal.	-	-
Total Variable	63,000	0.60
Fixed		
Labor 2/Shift x 60,000	120,000	1.14
Supervision	30,000	0.29
Maintenance Labor (1.3 % of Capital)	17,000	0.16
Maintenance Material (4 % of Capital)	51,000	0.49
Operating Supplies (0.5 % of Capital)	6,000	0.06
Overhead G & A (35 % of Total Labor)	58,000	0.55
Taxes & Insurance (3 % of Capital)	38,000	0.36
Total Fixed	320,000	3.05
Total Operating Costs	383,000	3.65

Table IV-12. OPERATING COST ESTIMATE - 300 T/D (cont.)

Offsite

Capital Cost Estimate $ 995,000

Operating Costs

	$/Year	$/Ton Dry Feed
Variable		
Electric Power		
300 KW x 24 x 3500 x 1¢/KWH	25,000	0.24
Fixed		
Labor 2/Shift x 60,000	120,000	1.14
Supervision	30,000	0.29
Maintenance Labor (1.3 % of Capital)	13,000	0.12
Maintenance Material (4 % of Capital)	40,000	0.38
Operating Supplies (0.5 % of Capital)	5,000	0.05
Overhead G & A (35 % of Total Labor)	57,000	0.54
Taxes & Insurance (3 % of Capital)	30,000	0.29
Total Fixed	295,000	2.81
Total Operating Costs	320,000	3.05

SECTION VIII

REFERENCES

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2. Finney, C.S., and Sotter, J.G., "Pyrolytic Oil From Tree Bark: Its Production and Combustion Properties", Presented to A.I. Ch. E. 77th Annual Meeting, Pittsburgh, Pa., June 3, 1974.

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APPENDIX A

ROYAL OAK CHARCOAL COMPANY

PROCESS CONTROL REPORT

Copies To: George W. Mallan, Garrett Research
G.B. Finney, Garrett Research
Matt Gould, C.P. Portland, Oregon
H.H. Powers, Royal Oak Charcoal

Number: 61
Location: Cookeville, Tn.
Date: 3-19-76
By: John Klish

Experimental briquets made with Pyrolytic Char from Garrett Research and Development Company

Garrett Research and Development Company, Inc.
1855 Carrion Rd.
La Verne, California 91750
Phone: 714-593-7481

Two lots consisting of 10 lbs. each of pyrolytic charcoal from wood bark was sent to Royal Oak Charcoal Company for evaluation as a raw material for making barbecue briquets. Briquets were made on a laboratory press and the following observations and conclusions were obtained.

Lot No. 1
26.0% Volatiles
9.5% Ash
64.5% Fixed Carbon

The extremely high volatile caused the char to be very spongy. Material required up to 15% starch to bind firm briquets. The briquets developed large cracks and splits when drying. Their appearance was bad.

The burning briquets smoked vigorously and had a disagreeable odor. The ash formed by the burning briquets was reddish-brown in color. This high volatile char is not suitable for barbecue briquets. Briquets were sent to Garrett Research for their evaluation.

Lot No. 2
7.6% Volatile
9.3% Ash
83.1% Fixed Carbon

This material briquetted very well with 7% starch binder. The briquets were firm and dried without developing cracks or splitting. The briquets ignited and burned well without any disagreeable odor, the ash is a grayish-brown which is normal for barbecue briquets. This char is suitable for manufacturing good quality barbecue briquets. Samples of these briquets have been sent to Garrett Research. Perhaps, the volatiles could be increased up to 15% and still have the desired properties to make a good charcoal briquet for barbecuing.

John Klish

John Klish
Process Control Manager

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APPENDIX B

SPECIAL REPORT FOR GARRETT RESEARCH AND DEVELOPMENT CO., INC.

Evaluation of Douglas Fir Bark Char as a Raw Material for Activated Carbon

St. Regis Technical Center
West Nyack, New York

SUMMARY

Three chars were supplied to St. Regis Paper Company by Garrett Research and Development Company, Inc. Through a preliminary evaluation, the best prospect of the three, as a raw material for activated carbon, was chosen for further study. This material was Douglas fir bark char. The reactivity in an activating gas, moisture, volatiles and ash contents of the three samples were very close. The Douglas fir sample had a significant difference between its measured nitrogen carbon dioxide surface areas and thus, probably has the largest micropore structure suitable for further activation.

Bulk density for the Garrett Douglas fir char was 0.271 g/cc untapped. Analyses indicated that the char contained impurities of essentially calcium, magnesium, silicon, aluminum and potassium.

Two additional batches of the material were supplied by Garrett Research and then blended. The chars being too fine for use in the equipment available necessitated compaction. Preliminary compaction attempts using coal tar pitch in a hot pellet press proved unsuccessful. Further work was performed following suggestions made by K. O. Industries. Lignosulfonate, protein colloid, coal tar pitch dispersed in octanol and coal tar pitch dispersed in octanol with acetone added to dissolve some additional pitch were used as binders. These materials were subjected to an activation step and most deteriorated significantly. Surface areas on the most promising materials indicated the pitch octanol dispersion though the best binder may have hindered pore development. The char has no coking properties, thus thermally induced agglomeration is not feasible.

An attempt was made to utilize the char in its supplied state but proved unsuccessful. Further work can be performed only if granular char is made available or a compaction procedure suitable for the char is developed.

October, 1973
V. Del Bagno

Approved:

Author:

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INTRODUCTION

Widely varied carbonaceous materials have historically been used for commercial production of activated carbons. These activated materials are characterized by having high void volumes and high surface areas as a consequence of which they adsorb large amounts of gases and vapors as compared to their volume. The same property also enables them to adsorb liquids and solids from solution. Depending on the porous structure and surface functional groups, activated carbons are classified into gas phase carbons, decolorizing carbons, water treatment carbons, etc. Today, most commercial carbons are produced from bituminous or lignite coals, petroleum sludges, coconut and nut shells, and paper mill wastes. By a suitable choice of production technique, an activated carbon can be made from any of these raw materials. The quality of the product, however, has been found to be greatly dependent upon the nature of the raw material when activated by currently used commercial processes.

Garrett Research and Development Co. Inc., developed a process which yields chars possibly suitable for the production of activated carbons. St. Regis evaluated a sample supplied by Garrett as a possible raw material for activated carbon.

This report contains the data developed by St. Regis. Four sections are contained herein. The first deals with a preliminary screening of three materials. Three samples were supplied by Garrett so that the most promising could be chosen for further extended work. The second section discusses the categorization of the char chosen as, potentially, the best raw material for activated carbon. The chemical reactivity in various activating gases was measured. An X-ray scan and metal analysis and sizing of the char were performed. Compaction and preliminary activation studies were made and the developed information is presented in section three. Conclusion and suggestions for further work are listed in section four.

PRELIMINARY MATERIAL EVALUATION

On May 3, 1973, St. Regis Paper Company contracted with Garrett Research and Development Company, Inc. to provide support to Garrett's work in the area of pyrolysis of industrial solid wastes under EPA Grant R-801207. The support was specifically to be in the evaluation, as a potential raw material for activated carbon, of char produced by Garrett.

Three samples of raw material manufactured from Douglas fir bark were shipped for prescreening and the most suitable as an activated carbon was chosen for further study. Of these three materials the best prospect as a raw material for activated carbon was that which, by a Garrett determination, contained 9.62% volatiles. Following St. Regis' procedures for volatile determination, the data did not correspond to that supplied by Garrett. However, duplication of Garrett's technique yielded very similar results. The procedure followed by Garrett (ASTM) can yield low values for volatile matter if these volatiles are driven off very slowly. The method used by St. Regis is thought to give a value which is more meaningful in evaluating the chars potential for activation.

The moisture, volatile matter, ash content, reaction rate in an activating medium, nitrogen and carbon dioxide surface areas were measured and the results are given in Table I.

The data indicated the three chars had similar volatile matter, ash content, and reactivity. Inspection of the laboratory data showed a larger amount of volatile matter given off below 600°C for the 9.62% sample over the 3.87% sample, although the total volatile matter was nearly the same at 850°C. As some preliminary pore development takes place by volatilization of material below 600°C, this factor indicated the 9.62% material might be more suitable for activated carbon than the 3.87%. The 21.03% volatile material appeared under microscopic study to be in the form of only slightly charred wood or bark. There would probably be minor, if any, advantage working with this over beginning with totally untreated raw material. The determination of nitrogen and carbon dioxide surface areas finally demonstrated that the 9.62% material was the most desirable. The difference between the nitrogen and carbon dioxide areas gives a qualitative indication of the micropore structure which may be utilized in further activation. This difference was 160 m^2/gm for the 9.62% material - the highest of the group.

Upon being informed of the decision to use 9.62% material for further work, Garrett Research provided two additional samples of this material, and the three samples were blended to ensure uniformity and supply a large batch for compaction.

TABLE I

[illegible]

[illegible]	Analysis			Reactivity Activation Rate @ [illegible]		Surface Area	
[illegible]	% [illegible]	% [illegible][1]	% ash	Gas	[illegible]	N_2 Area m^2/g	CO_2 Area m^2/g
3.87	3.8	33	38	[illegible] CO_2 Bal. N_2	.0072	10	90
9.62	3.8	33	35	[illegible] CO_2 Bal. N_2	.0032	20	180
22.83	3.8	25	35	[illegible] CO_2 Bal. N_2	.0073	8	40

---

[1] [illegible]

CHAR CATEGORIZATION

Sizing of the bark char supplied showed the material to be predominantly less than 120 mesh. Results of the sieve analysis are shown in Table II. Bulk density was found to be 0.271 g/cc untapped and 0.298 g/cc tapped. In addition to the reactivity analysis performed through preliminary screening of the material, additional determinations were made and this data is listed in Table III.

Following ASTM procedure D-388, Garrett material was found not to have any agglomerating character. An X-ray scan and atomic adsorption metal analysis of the char was performed and these results are shown in Table IV. High concentrations of calcium, magnesium and potassium are expected from barks. Phosphorus (P) level which was not measured should be close to magnesium. Traces of manganese, copper and zinc are also expected. The amounts of aluminum and iron along with some of the trace materials like nickel, chromium and strontium are unusual. These materials may represent some contamination from process equipment or chemicals used in the char production process.

TABLE II

SIEVE ANALYSIS OF DOUGLAS FIR BARK CHAR

SIEVE SIZE	% OF TOTAL WEIGHT REMAINING ON SCREEN
20	negligible
40	1.90
60	8.92
120	14.12
200	20.82
smaller than 200	54.24

TABLE III

REACTIVITY OF GARRETT DOUGLAS FIR BARK CHAR IN ACTIVATION MEDIA

Temperature (°C)	Gas Composition (Balance is N_2)	Reactivity (mg/mg - min.)
750	12% CO_2	.0018
750	53% CO_2	.0027
850	12% CO_2	.0073
850	53% CO_2	.0090
950	12% CO_2	.0125

TABLE IV

METAL ANALYSIS OF GARRETT CHAR

Metal	Detected by X-ray Scan (x)		Atomic Adsorption Analysis μg/g (as is basis)
	Raw Char	Ash	
Al	x	x	9260
Si	x	x	3670
P	x	x	Not measured
S	x	x	< 300
Cl	x	Not Detected	Not measured
K	x	x	4030
Ca	x	x	17200
Ti	x	x	360
Cr	Not measured	Not measured	37
Mn	x	x	913
Fe	x	x	8760
Ni	x	x	80
Cu	x	x	42
Zn	x	x	150
Sr	x	x	800
Ba	x	x	< 300
Na	Not measured	Not measured	629
Li	Not measured	Not measured	4
Mg	Not measured	Not measured	3280

COMPACTION AND ACTIVATION STUDIES

The Garrett material supplied was fine and of low density. An attempt was made to utilize the fine powder. Gas dispersion proved difficult and stabilization of proper flow patterns was impossible without carrying away large quantities of material from the reactor system. Thus compaction was required for the material to be utilized in St. Regis experimental furnaces. From a final product hardness standpoint the binder used should be less reactive than the base char. This enables activation to progress without deteriorating the pellet. The reactivity of carbonized coal tar pitch is 0.0005 mg/mg-min. compared to 0.9090 mg/mg-min. of the Garrett material. Both materials were reacted at 850°C and 53% carbon dioxide with the balance nitrogen.

Preliminary work using coal tar pitch as a binder and a pellet press at various conditions of temperature, pressure and binder concentration proved unsuccessful. Consultation with and experimentation by K. G. Industries in Chicago substantiated these findings. A liquid phase binder, particularly lignosulfonate pitch, was suggested. Work at West Nyack showed that the lignosulfonate pitch solution would pelletize, cure to a strong pellet, and withstand carbonization without deterioration. However, the carbonized binder is much more reactive than the base char and under mild conditions would burn off leaving the char powder unsupported by a binder matrix. These results are shown in Table V.

A summary of the results of the lignosulfonate binder study is given in Table VI. It was found that 35% by weight of total liquid solution had to be added to the char for proper final pellet strength. This solution was at an optimum effectiveness using 65% binder and 35% water. At a lower binder concentration in the solution, water oozed out of the pellet as pressure was applied. Above 65% the binder would not dissolve in the water.

A protein colloid binder was evaluated. This binder yields a higher uncured strength, lower final strength, but lower carbonized binder reactivity than lignosulfonate. An activation of this material at 750°C and 11% CO_2 for two hours yielded almost complete deterioration of the original granules. It should be noted that 11% CO_2 (balance nitrogen) at 750°C is a very mild condition for carbon activation.

The above results pointed to the necessity of developing a low reactivity binder system with high strength. Toward this end, two coal tar pitch dispersions were made. The first was a blend of octanol and coal tar pitch and the other was an octanol-acetone solution with coal tar pitch added. Pellets produced from octanol and pitch alone proved to be the strongest after carbonization and these were activated under the same conditions as the protein bound pellets. There was some deterioration of the pellets but considerably less than experienced when using the protein colloid or the lignosulfonate.

Nitrogen surface area measurements were made on the octanol-pitch bound char and the lignosulfonate bound char, both activated at 11% CO_2 at 750°C for two hours. These surface areas were 254 m^2/g and 336 m^2/g for the octanol-pitch and lignosulfonate bound material respectively. It appears that the octanol may hinder pore development. This is possible as the octanol may be able to be trapped by the char's pores and if unable to volatize rapidly out of the system will carbonize in place plugging the pores and thus hindering further surface area development.

Coal tar pitch and lignosulfonates are both inexpensive materials, i.e., approximately 8 and 5 cents/lb. respectively. A protein colloid binder would be economically feasible, commercially, only at very low binder levels as the cost is approximately 40 cents/lb. Organic dispersants such as octanol are quite expensive and would probably require a solvent recovery system if used in large quantities.

TABLE V

EVALUATION OF LIGNOSULFONATE PITCH STRENGTH DURING ACTIVATION

ACTIVATION CONDITIONS			PRODUCT CONDITION
Temperature	Time	Activating Gas	
850°C	3 hrs.	Flue Gas	Ashed
750°C	2 hrs.	11% CO_2, 89% N_2	Predominantly powder; the few large particles remaining were quite weak.
750°C	1 hr.	7% CO_2, 93% N_2	Similar to original material.

TABLE VI

LIGNOSULFONATE BINDER EVALUATION

Binder	Carbon Temperature	Cure Technique	After Carbonization
Water only	60°C	None	No Pelletization Obtainable
Lignosulfonate Solution			
5%[1] Binder	140°C	None	No Pelletization Obtainable
12%[1] Binder	140°C	100°C Preliminary Cure 177°C Final Cure	Weak Pellet
22%[1] Binder	140°C	None	Very weak pellet
22%[1] Binder	25°C	100°C Preliminary Cure 177°C Final Cure	Strong pellet

---

[1] Percentage based on char only. Water in binder solution not included.

CONCLUSIONS

1. Unless a suitable binder system is developed, Garrett char as supplied may be utilized only as a source of raw material for powdered activated carbon. Its very low density would make activation as a powder very difficult at best.

2. The ash content of the char is high. Thus activation at even a moderate burn off would yield a carbon with a very high ash. Acid washing of the char to lessen ash content would be beneficial for activation. The fact that ash content can affect binder efficiency and thus final product strength also points toward the need for study in this area.

3. Through activation of pelletized Garrett material nitrogen surface areas of 250 and 340 m^2/gm were obtained. This value is per gram of total material. On an ash free basis this area is 360 to 480 m^2/gm carbon.

4. No optimization to obtain the minimum binder level was performed. Binder levels of 22% in general are too high for commercialization. A typical commercial binder concentration is 6% but attempts to pelletize at this level were unsuccessful.

5. If the Garrett char production system was revamped to permit granular material to be formed, the necessity for compaction could possibly be eliminated.

APPENDIX C

PAPER COMPANY West Nyack Road, West Nyack, New York 10994

December 11, 1973

Mr. C. S. Finney
Assistant Manager
Solid Pollution Program
Garrett Research and Development Company, Inc.
1855 Carrion Road
La Verne, California 91750

Dear Mr. Finney:

On October 8, 1973, a sample of rice hull char was received. In response to your request to R. L. Miller, I performed a preliminary evaluation to determine if the char has potential for use as a raw material for activated carbon. The following are the results of the work accomplished.

Char Categorization

The physical and chemical properties of the char are shown in Table I. The volatile content is low and the ash very high. This ash level severely limits the chars' usefulness as a raw material for activated carbon. There is no agglomerating character inherent in the material and the nitrogen surface area though low, when taken on a per gram of carbon basis, is high for a raw char, namely 150 m^2/gm carbon. The bulk density of the rice hulls was greater than the Douglas Fir char but still rather low. Sieving of the material showed it to be predominantly less than 120 mesh. However, there was a more significant fraction above 40 mesh than was present with Douglas Fir char. This data is shown in Table II.

The reactivity of the rice hulls in activating gases is shown in Table III. This material was less reactive than the bark char. The activation rates are not normalized to an equal carbon basis. If normalization is performed, the rates for the rice hulls are still significantly lower. The lower reactivity may not be due to a difference in the carbon substrate but, rather to a blockage of the activating gas as a result of the high ash content. Two suitable materials for activated carbon are coal and petroleum cokes. They commonly have activation rates of .0011 and .0050 mg/mg-min respectively in an atmosphere of 53% CO_2 and at 853°C.

Under microscopic study, the rice hull char appeared to contain three distinct fractions, namely:

1. Semi-carbonized material consisting of large, flat thin particles.
2. Fully-carbonized material, consisting of short fibers of intermediate particle size.
3. Very small carbonized particles of spherical shape. The particles of this fraction were very friable.

These three fractions were separated in an attempt to isolate a low ash, volatile containing, fraction suitable for activation. The analysis of these are shown on Table IV. The 20 x 100 mesh cut had the highest volatile content, highest reactivity and lowest ash level. Unfortunately, the difference in ash contents were not as great as hoped; the ash concentration still being too high to make acid washing feasible even for the most promising cut.

At this point, it was apparent that the rice hull char as supplied was not a suitable raw material for activated carbon. Thus, quantitative atomic absorption analysis of the char and attempts to compact and activate the carbon were not made.

Conclusion

The high surface area of the carbon in the raw char from rice hulls and the suitable reactivity indicate it may be useful as a raw material for activated carbon if processing steps can be employed during char generation to minimize the ash level in the final product. However, in its present form, it is not suitable for this end use.

Very truly yours,

Vincent Del Bagno

VDB:dk:lp
Attachments

TABLE 1

Rice Hull Char Properties

Moisture:	2.0%
Volatile Content[1]:	7.6%
Ash:	73%
Impurities[2]:	Fe, Mn, Ti, Ca, K, Cl, S, P, Si, Ni, Cu, Zn
Agglomerating Character:	None
Nitrogen Surface Area (m^2/gm):	40
Bulk Density	
Tapped:	0.50gm/cc
Untapped:	0.34gm/cc

1. Determined with 850°C as a final temperature.

2. Given by qualitative X-ray scan. This technique cannot detect Na, Be, Mg, and Li. Elements obtained were identical for both the raw char and ashed material.

TABLE II

Sieve Analysis of Rice Hull Char

Sieve Size	% of Total Weight Remaining On Screen
20	0
40	8.0
60	5.3
120	12.2
200	22.8
Less than 200	51.7

TABLE III

Reactivity of Garrett Rice Hull Char in Activation Media

Conditions		
Temperature °C	Gas Composition (Balance Is Nitrogen)	Reactivity (mg/mg-min)
750	12% CO_2	.0002
750	53% CO_2	.0010
850	12% CO_2	.0009
850	53% CO_2	.0013
950	12% CO_2	.0041

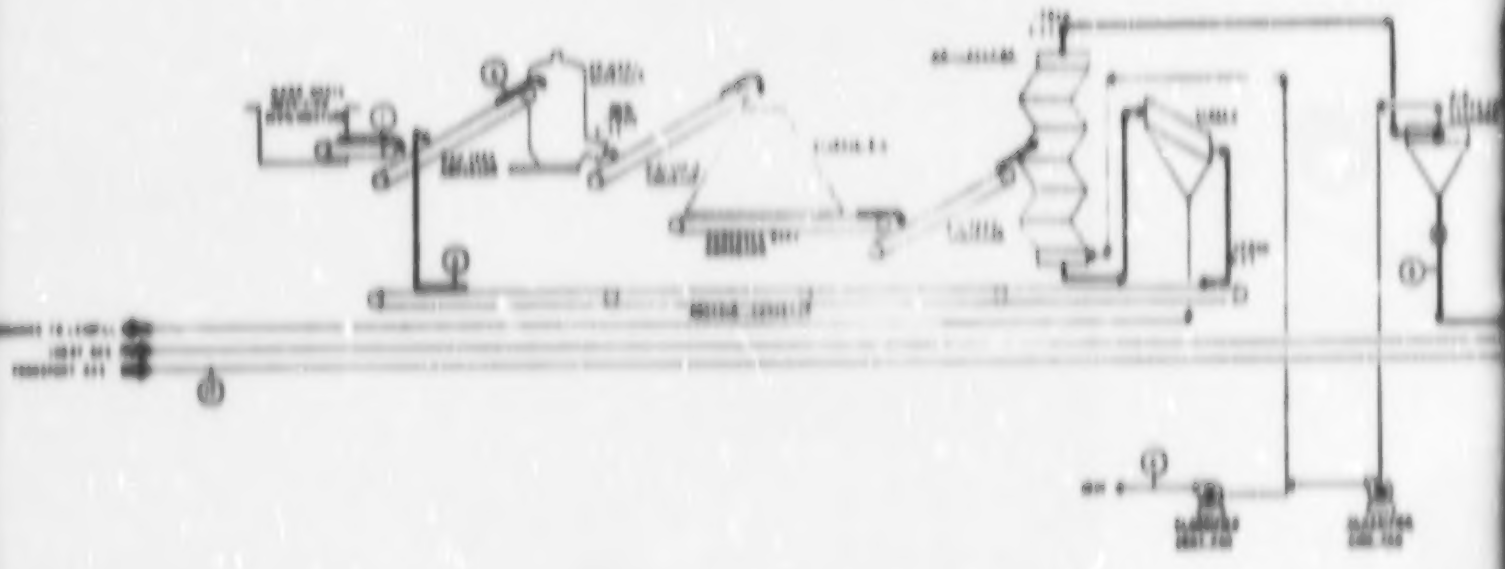
TABLE IV

Properties of Three Rice Hull Char Sieve Fractions

Sieve Fraction	Volatile Content	Reactivity @ 850°C & 53% CO_2 (mg/mg-min.)	Ash
20 x 100	12.4%	.0024	55%
100 x 200	7.2%	.0016	69%
Less than 200	6.1%	.0015	75%

APPENDIX D

Copies of Appendix D entitled "Combustion Tests of Pyrolytic Oils made from Solid Waste Materials" by KVB, Tustin, California, can be obtained upon request from Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268.



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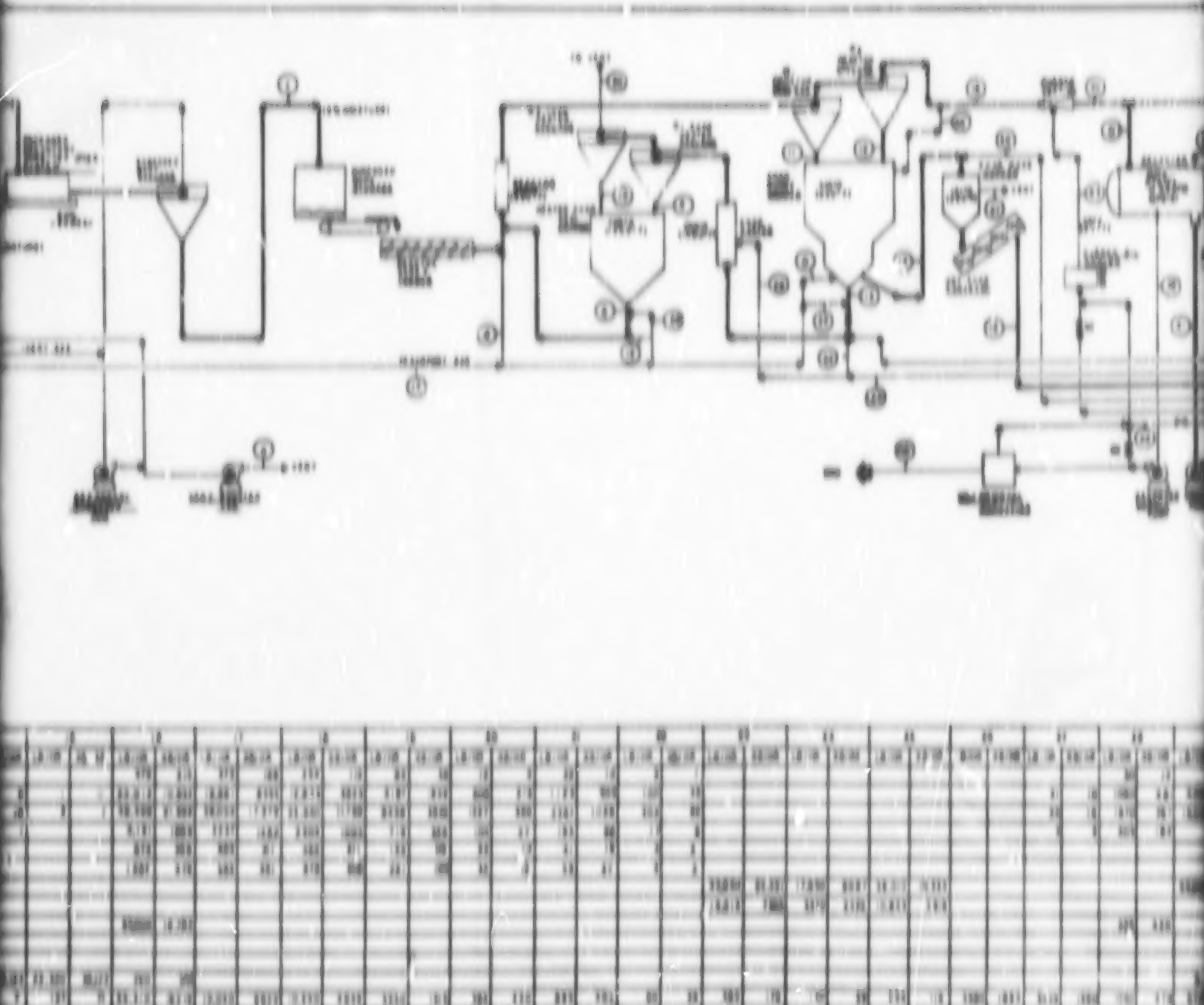
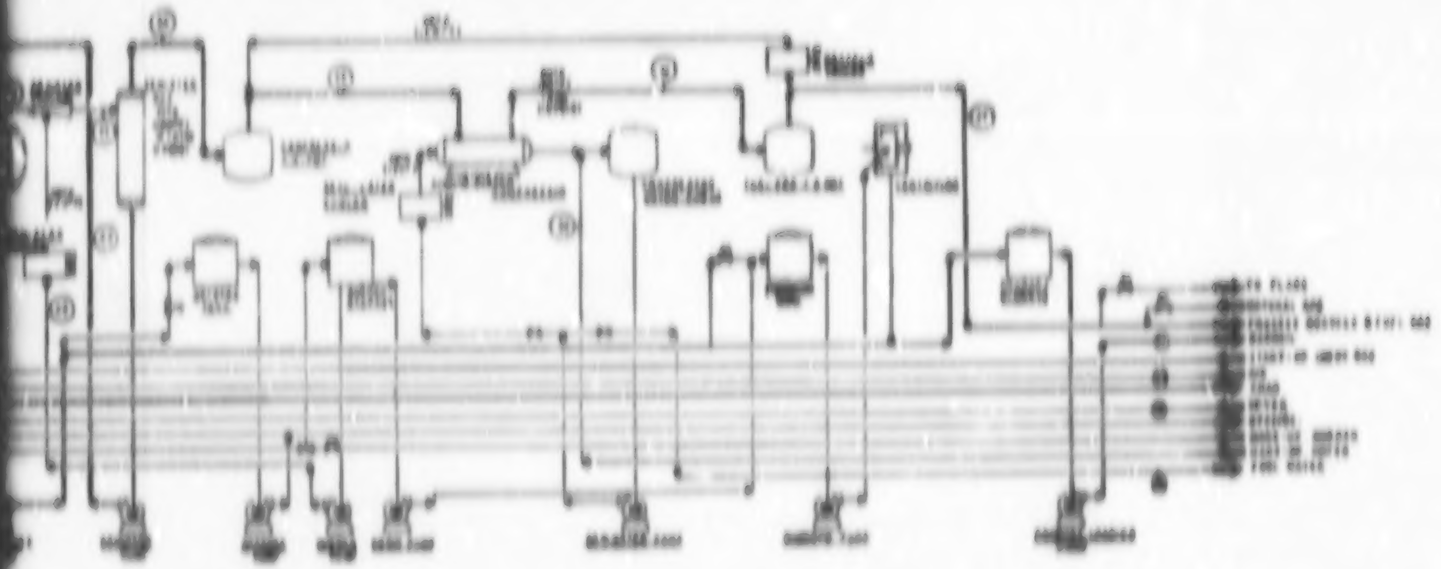


Figure IV-1. TREE BARK PYROLYSIS PROCESS FLOW DIAGRAM AND MATERIAL



ALANCE.